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**Erben et al.**(10) **Pub. No.: US 2007/0146835 A1**(43) **Pub. Date: Jun. 28, 2007**(54) **METHODS FOR MAKING HOLOGRAPHIC  
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(57)

**ABSTRACT**

A method of making a holographic data storage medium is provided. The method comprises: (a) providing an optically transparent substrate comprising at least one photochemically active dye; and (b) irradiating the optically transparent substrate at at least one wavelength at which the optically transparent substrate has an absorbance in a range from about 0.1 to 1, to produce a modified optically transparent substrate comprising at least one optically readable datum and at least one photo-product of the photochemically active dye. The at least one wavelength is in a range from about 300 nanometers to about 800 nanometers. The optically transparent substrate is at least 100 micrometers thick, and comprises the photochemically active dye in an amount corresponding to from about 0.1 to about 10 weight percent based on a total weight of the optically transparent substrate.

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## METHODS FOR MAKING HOLOGRAPHIC DATA STORAGE ARTICLES

### BACKGROUND

[0001] The present disclosure relates to methods for making and using holographic data storage articles. Further, the disclosure relates to holographic data storage articles.

[0002] Holographic storage is the storage of data in the form of holograms, which are images of three dimensional interference patterns created by the intersection of two beams of light, in a photosensitive medium. The superposition of a signal beam, which contains digitally encoded data, and a reference beam forms an interference pattern within the volume of the medium resulting in a chemical reaction that changes or modulates the refractive index of the medium. This modulation serves to record as the hologram both the intensity and phase information from the signal. The hologram can later be retrieved by exposing the storage medium to the reference beam alone, which interacts with the stored holographic data to generate a reconstructed signal beam proportional to the initial signal beam used to store the holographic image. Thus, in holographic data storage, data is stored throughout the volume of the medium via three dimensional interference patterns.

[0003] Each hologram may contain anywhere from one to  $1 \times 10^6$  or more bits of data. One distinct advantage of holographic storage over surface-based storage formats, including CDs or DVDs, is that a large number of holograms may be stored in an overlapping manner in the same volume of the photosensitive medium using a multiplexing technique, such as by varying the signal and/or reference beam angle, wavelength, or medium position. However, a major impediment towards the realization of holographic storage as a viable technique has been the development of a reliable and economically feasible storage medium.

[0004] Early holographic storage media employed inorganic photo-refractive crystals, such as doped or un-doped lithium niobate ( $\text{LiNbO}_3$ ), in which incident light creates refractive index changes. These index changes are due to the photo-induced creation and subsequent trapping of electrons leading to an induced internal electric field that ultimately modifies the refractive index through a linear electro-optic effect. However,  $\text{LiNbO}_3$  is expensive, exhibits relatively poor efficiency, fades over time, and requires thick crystals to observe any significant index changes.

[0005] More recent work has led to the development of polymers that can sustain larger refractive index changes owing to optically induced polymerization processes. These materials, which are referred to as photopolymers, have significantly improved optical sensitivity and efficiency relative to  $\text{LiNbO}_3$  and its variants. In prior art processes, "single-chemistry" systems have been employed, wherein the media comprise a homogeneous mixture of at least one photo-active polymerizable liquid monomer or oligomer, an initiator, an inert polymeric filler, and optionally a sensitizer. Since it initially has a large fraction of the mixture in monomeric or oligomeric form, the medium may have a gel-like consistency that necessitates an ultraviolet (UV) curing step to provide form and stability. Unfortunately, the UV curing step may consume a large portion of the photo-active monomer or oligomer, leaving significantly less photo-active monomer or oligomer available for data stor-

age. Furthermore, even under highly controlled curing conditions, the UV curing step may often result in variable degrees of polymerization and, consequently, poor uniformity among media samples.

[0006] Dye-doped data storage materials based on polymeric materials have been developed. The sensitivity of a dye-doped data storage material is dependent upon the concentration of the dye, the dye's absorption cross-section at the recording wavelength, the quantum efficiency of the photochemical transition, and the index change of the dye molecule for a unit dye density. However, as the product of dye concentration and the absorption cross-section increases, the storage medium (for example, an optical data storage disc) becomes opaque, which complicates both recording and readout.

[0007] Therefore, there is a need for holographic data storage methods whereby high volumetric data storage capacities can be achieved using photochemically active dyes that are efficient and sensitive to electromagnetic energy, such as light without interference from the main absorption peak of the dye.

### SUMMARY

[0008] Disclosed herein are methods for producing and using holographic data storage media, which are valuable for reliably storing large amount of data.

[0009] In one aspect, the present invention is a method of making a holographic data storage medium. The method comprises: (a) providing an optically transparent substrate comprising at least one photochemically active dye; and (b) irradiating the optically transparent substrate at at least one wavelength at which the optically transparent substrate has an absorbance in a range from about 0.1 to 1, to produce a modified optically transparent substrate comprising at least one optically readable datum and at least one photo-product of the photochemically active dye. The at least one wavelength is in a range from about 300 nanometers to about 800 nanometers. The optically transparent substrate is at least 100 micrometers thick, and comprises the photochemically active dye in an amount corresponding to from about 0.1 to about 10 weight percent based on a total weight of the optically transparent substrate.

[0010] In another aspect of the present invention, an optical writing and reading method is provided. The method comprises irradiating a holographic data storage medium with a signal beam possessing data (or at least one datum) and a reference beam simultaneously to partly convert the photochemically active dye into at least one photo-product and store the data in the signal beam as a hologram in the holographic data storage medium. The holographic storage medium comprises an optically transparent substrate and at least one photochemically active dye. The optically transparent substrate has a thickness of at least 100 micrometers, and comprises the photochemically active dye in an amount corresponding to from about 0.1 to about 10 weight percent based on a total weight of the optically transparent substrate, and a UV-visible absorbance in a range from about 0.1 to 1 at at least one wavelength in a range from about 300 nanometers to about 800 nanometers. Then the holographic storage medium is irradiated with a read beam and the data contained by diffracted light from the hologram is read. In an embodiment, conversion of the photochemically active

dye to at least one photo-product occurs such that the data storage medium comprises the dye as well as the photo-product to provide the refractive index contrast needed to produce the hologram.

[0011] In yet another aspect, the present invention is a method for using a holographic data storage article. The method comprises irradiating a holographic data storage medium in the holographic data storage article with electromagnetic energy having a first wavelength. The holographic data storage medium comprises an optically transparent substrate that is at least 100 micrometers thick, and comprises at least one photochemically active dye in an amount corresponding to from about 0.1 to about 10 weight percent based on a total weight of the optically transparent substrate. The irradiation is done at at least one wavelength in a range from about 300 nanometers to about 800 nanometers at which the optically transparent substrate has a UV-visible absorbance in a range from about 0.1 to 1. A modified optically transparent substrate comprising at least one photo-product of the at least one photochemically active dye, and at least one optically readable datum stored as a hologram is formed. Then the modified optically transparent substrate is irradiated with electromagnetic energy having a second wavelength to read the hologram.

[0012] In still yet another aspect, the present invention is a method for manufacturing a holographic data storage medium. The method comprises forming a film of an optically transparent substrate comprising at least one optically transparent plastic material and at least one photochemically active dye having a UV-visible absorbance in a range between about 0.1 and about 1 at a wavelength in a range between about 300 nanometers and about 800 nanometers, said film having a thickness of at least 100 micrometers; wherein the optically transparent substrate comprises from about 0.1 to about 10 weight percent of the optically transparent substrate.

[0013] In another aspect, the present invention is a holographic data storage medium. The holographic data storage medium comprises an optically transparent substrate comprising at least one optically transparent plastic material, at least one photochemically active dye, and at least one photo-product thereof. The at least one photo-product is patterned within the optically transparent substrate to provide at least one optically readable datum comprised within the holographic storage medium. The optically transparent substrate is at least 100 micrometers thick and comprises the photochemically active dye in an amount corresponding to from about 0.1 to about 10 weight percent based on a total weight of the optically transparent substrate. The optically transparent substrate has a UV-visible absorbance in a range from about 0.1 to 1 at at least one wavelength in a range from about 300 nanometers to about 800 nanometers.

[0014] These and other features, aspects, and advantages of the present invention may be more understood more readily by reference to the following detailed description.

#### DETAILED DESCRIPTION

[0015] Some aspects of the present invention and general scientific principles used herein can be more clearly understood by referring to U.S. Patent Application 2005/0136333 (Ser. No. 10,742,461), which was published on Jun. 23,

2005; and co-pending application having Ser. No. 10/954,779, filed on Sep. 30, 2004; both which are incorporated herein in their entirety.

[0016] As defined herein, the term M/# denotes the capacity of a data storage medium, and can be measured as a function of the total number of multiplexed holograms that can be recorded at a volume element of the data storage medium at a given diffraction efficiency. M/# depends upon various parameters, such as the change in refractive index ( $\Delta n$ ), the thickness of the medium, and the dye concentration. These terms are described further in this disclosure. The M/# is defined as shown in equation (1):

$$M/\# = \sum_{i=1}^N \sqrt{\eta_i} \quad \text{Equation (1)}$$

where  $\eta_i$  is diffraction efficiency of the  $i^{\text{th}}$  hologram, and N is the number of recorded holograms. The experimental setup for M/# measurement for a test sample at a chosen wavelength, for example, at 532 nanometers or 405 nanometers involves positioning the testing sample on a rotary stage that is controlled by a computer. The rotary stage has a high angular resolution, for example, about 0.0001 degree. An M/# measurement involves two steps: recording and readout. At recording, multiple planewave holograms are recorded at the same location on the same sample. A plane wave hologram is a recorded interference pattern produced by a signal beam and a reference beam. The signal and reference beams are coherent to each other. They are both planewaves that have the same power and beam size, incident at the same location on the sample, and polarized in the same direction. Multiple planewave holograms are recorded by rotating the sample. Angular spacing between two adjacent holograms is about 0.2 degree. This spacing is chosen so that their impact to the previously recorded holograms, when multiplexing additional holograms, is minimal and at the same time, the usage of the total capacity of the media is efficient. Recording time for each hologram is generally the same in M/# measurements. At readout, the signal beam is blocked. The diffracted signal is measured using the reference beam and an amplified photo-detector. Diffracted power is measured by rotating the sample across the recording angle range with a step size of about 0.004 degree. The power of the reference beam used for readout is typically about 2-3 orders of magnitude smaller than that used at recording. This is to minimize hologram erasure during readout while maintaining a measurable diffracted signal. From the diffracted signal, the multiplexed holograms can be identified from the diffraction peaks at the hologram recording angles. The diffraction efficiency of the  $i^{\text{th}}$  hologram,  $\eta_i$ , is then calculated by using equation (2):

$$\eta_i = \frac{P_{i, \text{diffracted}}}{P_{\text{reference}}} \quad \text{Equation (2)}$$

where  $P_{i, \text{diffracted}}$  is the diffracted power of the  $i^{\text{th}}$  hologram. M/# is then calculated using the diffraction efficiencies of the holograms and equation (1). Thus, a holographic plane wave characterization system may be used to test the character-

istics of the data storage material, especially multiplexed holograms. Further, the characteristics of the data storage material can also be determined by measuring the diffraction efficiency.

[0017] As defined herein, the term “volume element” means a three dimensional portion of the total volume of an optically transparent substrate or a modified optically transparent substrate.

[0018] As defined herein, the term “optically readable datum” can be understood as being made up of one or more volume elements of a first or a modified optically transparent substrate containing a “hologram” of the data to be stored. The refractive index within an individual volume element may be constant throughout the volume element, as in the case of a volume element that has not been exposed to electromagnetic radiation, or in the case of a volume element in which the photochemically active dye has been reacted to the same degree throughout the volume element. It is believed that most volume elements that have been exposed to electromagnetic radiation during the holographic data writing process will contain a complex holographic pattern and as such the refractive index within the volume element will vary across the volume element. In instances in which the refractive index within the volume element varies across the volume element, it is convenient to regard the volume element as having an “average refractive index” which may be compared to the refractive index of the corresponding volume element prior to irradiation. Thus, in one embodiment an optically readable datum comprises at least one volume element having a refractive index that is different from a (the) corresponding volume element of the optically transparent substrate prior to irradiation. Data storage is achieved by locally changing the refractive index of the data storage medium in a graded fashion (continuous sinusoidal variations), rather than discrete steps, and then using the induced changes as diffractive optical elements.

[0019] The capacity to store data as holograms (M/#) is also directly proportional to the ratio of the change in refractive index per unit dye density ( $\Delta n/N_0$ ) at the wavelength used for reading the data to the absorption cross section ( $\sigma$ ) at a given wavelength used for writing the data as a hologram. The refractive index change per unit dye density is given by the ratio of the difference in refractive index of the volume element before irradiation minus the refractive index of the same volume element after irradiation to the density of the dye molecules. The refractive index change per unit dye density has a unit of (centimeter)<sup>3</sup>. Thus in an embodiment, the optically readable datum comprises at least one volume element wherein the ratio of the change in the refractive index per unit dye density of the at least one volume element to an absorption cross section of the at least one photochemically active dye is at least about 10<sup>-5</sup> expressed in units of centimeter.

[0020] Sensitivity (S) is a measure of the diffraction efficiency of a hologram recorded using a certain amount of light fluence (F). The light fluence (F) is given by the product of light intensity (I) and recording time (t). Mathematically, sensitivity is given by equation (3),

$$S = \frac{\sqrt{\eta}}{I \cdot t \cdot L} (\text{cm}/\text{J}) \quad \text{Equation (3)}$$

wherein I is the intensity of the recording beam, “t” is the recording time, L is the thickness of the recording (or data storage) medium (example, disc), and  $\eta$  is the diffraction efficiency. Diffraction efficiency is given by equation (4),

$$\eta = \sin^2 \left( \frac{\pi \cdot \Delta n \cdot L}{\lambda \cdot \cos(\theta)} \right) \quad \text{Equation (4)}$$

wherein  $\lambda$  is the wavelength of light in the recording medium,  $\theta$  is the recording angle in the media, and  $\Delta n$  is the refractive index contrast of the grating, which is produced by the recording process, wherein the dye molecule undergoes a photochemical conversion.

[0021] The absorption cross section is a measurement of an atom or molecule’s ability to absorb light at a specified wavelength, and is measured in square cm/molecule. It is generally denoted by  $\sigma(\lambda)$  and is governed by the Beer-Lambert Law for optically thin samples as shown in Equation (5),

$$\sigma(\lambda) = \ln(10) \cdot \frac{\text{Absorbance}(\lambda)}{N_0 \cdot L} (\text{cm}^2) \quad \text{Equation (5)}$$

wherein  $N_0$  is the concentration in molecules per cubic centimeter, and L is the sample thickness in centimeters.

[0022] Quantum efficiency (QE) is a measure of the probability of a photochemical transition for each absorbed photon of a given wavelength. Thus, it gives a measure of the efficiency with which incident light is used to achieve a given photochemical conversion, also called as a bleaching process. QE is given by equation (6),

$$QE = \frac{hc/\lambda}{\sigma \cdot F_0} \quad \text{Equation (6)}$$

wherein “h” is the Planck’s constant, “c” is the velocity of light,  $\sigma(\lambda)$  is the absorption cross section at the wavelength  $\lambda$ , and  $F_0$  is the bleaching fluence. The parameter  $F_0$  is given by the product of light intensity (I) and a time constant ( $\tau$ ) that characterizes the bleaching process.

[0023] The term “optically transparent” as applied to an optically transparent substrate or an optically transparent plastic material means that they have an absorbance of less than 1, that is at least 10 percent of incident light is transmitted through the material at at least one wavelength in a range between about 300 and about 800 nanometers.

[0024] As defined herein, the term “an optically transparent substrate” denotes a combination of an optically transparent plastic material and at least one photochemically active dye, which has an absorbance of less than 1, that is,

at least 10 percent of incident light is transmitted through the material at at least one wavelength in a range between about 300 and about 800 nanometers.

**[0025]** As defined herein, the term “optically transparent plastic material” means a plastic material which has an absorbance of less than 1, that is, at least 10 percent of incident light is transmitted through the material) at at least one wavelength in a range between about 300 and about 800 nanometers.

**[0026]** As used herein the term “aliphatic radical” refers to an organic radical having a valence of at least one consisting of a linear or branched array of atoms which is not cyclic. Aliphatic radicals are defined to comprise at least one carbon atom. The array of atoms comprising the aliphatic radical may include heteroatoms such as nitrogen, sulfur, silicon, selenium and oxygen or may be composed exclusively of carbon and hydrogen. For convenience, the term “aliphatic radical” is defined herein to encompass, as part of the “linear or branched array of atoms which is not cyclic” a wide range of functional groups such as alkyl groups, alkenyl groups, alkynyl groups, haloalkyl groups, conjugated dienyl groups, alcohol groups, ether groups, aldehyde groups, ketone groups, carboxylic acid groups, acyl groups (for example carboxylic acid derivatives such as esters and amides), amine groups, nitro groups, and the like. For example, the 4-methylpent-1-yl radical is a  $C_6$  aliphatic radical comprising a methyl group, the methyl group being a functional group which is an alkyl group. Similarly, the 4-nitrobut-1-yl group is a  $C_4$  aliphatic radical comprising a nitro group, the nitro group being a functional group. An aliphatic radical may be a haloalkyl group which comprises one or more halogen atoms which may be the same or different. Halogen atoms include, for example; fluorine, chlorine, bromine, and iodine. Aliphatic radicals comprising one or more halogen atoms include the alkyl halides trifluoromethyl, bromodifluoromethyl, chlorodifluoromethyl, hexafluoroisopropylidene, chloromethyl, difluorovinylidene, trichloromethyl, bromodichloromethyl, bromoethyl, 2-bromotrimethylene (e.g.,  $-CH_2CHBrCH_2-$ ), and the like. Further examples of aliphatic radicals include allyl, aminocarbonyl (i.e.,  $-CONH_2$ ), carbonyl, 2,2-dicyanoisopropylidene (i.e.,  $-CH_2C(CN)_2CH_2-$ ), methyl (i.e.,  $-CH_3$ ), methylene (i.e.,  $-CH_2-$ ), ethyl, ethylene, formyl (i.e.,  $-CHO$ ), hexyl, hexamethylene, hydroxymethyl (i.e.,  $-CH_2OH$ ), mercaptomethyl (i.e.,  $-CH_2SH$ ), methylthio (i.e.,  $-SCH_3$ ), methylthiomethyl (i.e.,  $-CH_2SCH_3$ ), methoxy, methoxycarbonyl (i.e.,  $CH_3OCO-$ ), nitromethyl (i.e.,  $-CH_2NO_2$ ), thiocarbonyl, trimethylsilyl (i.e.,  $(CH_3)_3Si-$ ), t-butyldimethylsilyl, 3-trimethoxysilylpropyl (i.e.,  $(CH_3O)_3SiCH_2CH_2CH_2-$ ), vinyl, vinylidene, and the like. By way of further example, a  $C_1$ - $C_{10}$  aliphatic radical contains at least one but no more than 10 carbon atoms. A methyl group (i.e.,  $CH_3-$ ) is an example of a  $C_1$  aliphatic radical. A decyl group (i.e.,  $CH_3(CH_2)_9-$ ) is an example of a  $C_{10}$  aliphatic radical.

**[0027]** As used herein, the term “aromatic radical” refers to an array of atoms having a valence of at least one comprising at least one aromatic group. The array of atoms having a valence of at least one comprising at least one aromatic group may include heteroatoms such as nitrogen, sulfur, selenium, silicon and oxygen, or may be composed exclusively of carbon and hydrogen. As used herein, the term “aromatic radical” includes but is not limited to phenyl,

pyridyl, furanyl, thienyl, naphthyl, phenylene, and biphenyl radicals. As noted, the aromatic radical contains at least one aromatic group. The aromatic group is invariably a cyclic structure having  $4n+2$  “delocalized” electrons where “n” is an integer equal to 1 or greater, as illustrated by phenyl groups ( $n=1$ ), thienyl groups ( $n=1$ ), furanyl groups ( $n=1$ ), naphthyl groups ( $n=2$ ), azulenyl groups ( $n=2$ ), anthracenyl groups ( $n=3$ ) and the like. The aromatic radical may also include nonaromatic components. For example, a benzyl group is an aromatic radical that comprises a phenyl ring (the aromatic group) and a methylene group (the nonaromatic component). Similarly a tetrahydronaphthyl radical is an aromatic radical comprising an aromatic group ( $C_6H_5$ ) fused to a nonaromatic component  $-(CH_2)_4-$ . For convenience, the term “aromatic radical” is defined herein to encompass a wide range of functional groups such as alkyl groups, alkenyl groups, alkynyl groups, haloalkyl groups, haloaromatic groups, conjugated dienyl groups, alcohol groups, ether groups, aldehydes groups, ketone groups, carboxylic acid groups, acyl groups (for example carboxylic acid derivatives such as esters and amides), amine groups, nitro groups, and the like. For example, the 4-methylphenyl radical is a  $C_7$  aromatic radical comprising a methyl group, the methyl group being a functional group which is an alkyl group. Similarly, the 2-nitrophenyl group is a  $C_6$  aromatic radical comprising a nitro group, the nitro group being a functional group. Aromatic radicals include halogenated aromatic radicals such as 4-trifluoromethylphenyl, hexafluoroisopropylidenebis(4-phen-1-yloxy) (i.e.,  $-OPhC(CF_3)_2PhO-$ ), 4-chloromethylphen-1-yl, 3-trifluorovinyl-2-thienyl, 3-trichloromethylphen-1-yl (i.e.,  $3-CCl_3Ph-$ ), 4-(3-bromoprop-1-yl)phen-1-yl (i.e.,  $4-BrCH_2CH_2CH_2Ph-$ ), and the like. Further examples of aromatic radicals include 4-allyloxyphen-1-oxy, 4-aminophen-1-yl (i.e.,  $4-H_2NPh-$ ), 3-aminocarbonylphen-1-yl (i.e.,  $NH_2COPh-$ ), 4-benzoylphen-1-yl, dicyanomethylidenebis(4-phen-1-yloxy) (i.e.,  $-OPhC(CN)_2PhO-$ ), 3-methylphen-1-yl, methylenebis(4-phen-1-yloxy) (i.e.,  $-OPhCH_2PhO-$ ), 2-ethylphen-1-yl, phenylethenyl, 3-formyl-2-thienyl, 2-hexyl-5-furanyl, hexamethylene-1,6-bis(4-phen-1-yloxy) (i.e.,  $-OPh(CH_2)_6PhO-$ ), 4-hydroxymethylphen-1-yl (i.e.,  $4-HOCH_2Ph-$ ), 4-mercaptopmethylphen-1-yl (i.e.,  $4-HSCH_2Ph-$ ), 4-methylthiophen-1-yl (i.e.,  $4-CH_3SPh-$ ), 3-methoxyphen-1-yl, 2-methoxycarbonylphen-1-yloxy (e.g., methyl salicyl), 2-nitromethylphen-1-yl (i.e.,  $2-NO_2CH_2Ph$ ), 3-trimethylsilylphen-1-yl, 4-t-butyldimethylsilylphen-1-yl, 4-vinylphen-1-yl, vinylidenebis(phenyl), and the like. The term “a  $C_3$ - $C_{10}$  aromatic radical” includes aromatic radicals containing at least three but no more than 10 carbon atoms. The aromatic radical 1-imidazolyl ( $C_3H_2N_2-$ ) represents a  $C_3$  aromatic radical. The benzyl radical ( $C_7H_7-$ ) represents a  $C_7$  aromatic radical.

**[0028]** As used herein the term “cycloaliphatic radical” refers to a radical having a valence of at least one, and comprising an array of atoms which is cyclic but which is not aromatic. As defined herein a “cycloaliphatic radical” does not contain an aromatic group. A “cycloaliphatic radical” may comprise one or more noncyclic components. For example, a cyclohexylmethyl group ( $C_6H_{11}CH_2-$ ) is a cycloaliphatic radical which comprises a cyclohexyl ring (the array of atoms which is cyclic but which is not aromatic) and a methylene group (the noncyclic component). The cycloaliphatic radical may include heteroatoms such as

nitrogen, sulfur, selenium, silicon and oxygen, or may be composed exclusively of carbon and hydrogen. For convenience, the term "cycloaliphatic radical" is defined herein to encompass a wide range of functional groups such as alkyl groups, alkenyl groups, alkynyl groups, haloalkyl groups, conjugated dienyl groups, alcohol groups, ether groups, aldehyde groups, ketone groups, carboxylic acid groups, acyl groups (for example carboxylic acid derivatives such as esters and amides), amine groups, nitro groups, and the like. For example, the 4-methylcyclopent-1-yl radical is a  $C_6$  cycloaliphatic radical comprising a methyl group, the methyl group being a functional group which is an alkyl group. Similarly, the 2-nitrocyclobut-1-yl radical is a  $C_4$  cycloaliphatic radical comprising a nitro group, the nitro group being a functional group. A cycloaliphatic radical may comprise one or more halogen atoms which may be the same or different. Halogen atoms include, for example; fluorine, chlorine, bromine, and iodine. Cycloaliphatic radicals comprising one or more halogen atoms include 2-trifluoromethylcyclohex-1-yl, 4-bromodifluoromethylcyclooct-1-yl, 2-chlorodifluoromethylcyclohex-1-yl, hexafluoroisopropylidene-2,2-bis(cyclohex-4-yl) (i.e.,  $-C_6H_{10}C(CF_3)_2C_6H_{10}-$ ), 2-chloromethylcyclohex-1-yl, 3-difluoromethylenecyclohex-1-yl, 4-trichloromethylcyclohex-1-yloxy, 4-bromodichloromethylcyclohex-1-ylthio, 2-bromoethylcyclopent-1-yl, 2-bromopropylcyclohex-1-yloxy (e.g.,  $CH_3CHBrCH_2C_6H_{10}O-$ ), and the like. Further examples of cycloaliphatic radicals include 4-allyloxycyclohex-1-yl, 4-aminocyclohex-1-yl (i.e.,  $H_2NC_6H_{10}-$ ), 4-aminocarbonylcyclopent-1-yl (i.e.,  $NH_2COC_5H_8-$ ), 4-acetyloxycyclohex-1-yl, 2,2-dicyanoisopropylidenebis(cyclohex-4-yloxy) (i.e.,  $-OC_6H_{10}C(CN)_2C_6H_{10}O-$ ), 3-methylcyclohex-1-yl, methylenebis(cyclohex-4-yloxy) (i.e.,  $-OC_6H_{10}CH_2C_6H_{10}O-$ ), 1-ethylcyclobut-1-yl, cyclopropylethenyl, 3-formyl-2-terahydrofuran-1-yl, 2-hexyl-5-tetrahydrofuran-1-yl, hexamethylene-1,6-bis(cyclohex-4-yloxy) (i.e.,  $-OC_6H_{10}(CH_2)_6C_6H_{10}O-$ ), 4-hydroxymethylcyclohex-1-yl (i.e.,  $4-HOCH_2C_6H_{10}-$ ), 4-mercaptomethylcyclohex-1-yl (i.e.,  $4-HSCH_2C_6H_{10}-$ ), 4-methylthiocyclohex-1-yl (i.e.,  $4-CH_3SC_6H_{10}-$ ), 4-methoxycyclohex-1-yl, 2-methoxycarbonylcyclohex-1-yloxy ( $2-CH_3OCOC_6H_{10}O-$ ), 4-nitromethylcyclohex-1-yl (i.e.,  $NO_2CH_2C_6H_{10}-$ ), 3-trimethylsilylcyclohex-1-yl, 2-*t*-butyldimethylsilylcyclopent-1-yl, 4-trimethoxysilylthylcyclohex-1-yl (e.g.,  $(CH_3O)_3SiCH_2CH_2C_6H_{10}-$ ), 4-vinylcyclohex-1-yl, vinylidenebis(cyclohexyl), and the like. The term "a  $C_3-C_{10}$  cycloaliphatic radical" includes cycloaliphatic radicals containing at least three but no more than 10 carbon atoms. The cycloaliphatic radical 2-tetrahydrofuran-1-yl ( $C_4H_7O-$ ) represents a  $C_4$  cycloaliphatic radical. The cyclohexylmethyl radical ( $C_6H_{11}CH_2-$ ) represents a  $C_7$  cycloaliphatic radical.

[0029] The present invention provides methods for optical data storage use in holographic data storage and retrieval. These holographic storage media include an optically transparent substrate comprising an optically transparent plastic material and at least one photochemically active dye. The photochemically active dye has desirable optical properties, such as a relatively low absorption cross-section while having a relatively high refractive index change and/or relatively high quantum efficiency. High quantum efficiency also leads to a higher sensitivity since sensitivity is directly proportional to the product of quantum efficiency and refractive index change (defined as  $\Delta n$ ). Writing of data as a

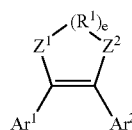
hologram into the optically transparent substrate comprising the photochemical dye is due to the dye undergoing a photochemical conversion at the write wavelength, thereby producing a modified optically transparent substrate comprising at least one optically readable datum. The sensitivity of a dye-doped data storage material is dependent upon the concentration of the dye ( $N_0$ ), the dye's absorption cross-section at the recording wavelength, the quantum efficiency QE of the photochemical transition, and the index change of the dye molecule for a unit dye density ( $\Delta n_0/N_0$ ). However, as the product of dye concentration and the absorption cross-section increases, the disc becomes opaque, which complicates both recording and readout. Therefore, dyes of interest for achieving high M/#s are those materials that undergo a partial photochemical transformation accompanied with a high refractive index change and a high quantum efficiency at the wavelength that is used for writing data, one that is removed from the main UV-visible absorption peak of the dye.

[0030] A photochemically active dye may be described as a dye molecule that has an optical absorption resonance characterized by a center wavelength associated with the maximum absorption and a spectral width (full width at half of the maximum, FWHM) of less than 500 nanometers (hereinafter abbreviated as "nm"). In addition, the photochemically active dye molecule undergoes a partial light induced chemical reaction when exposed to light with a wavelength within the absorption range to form at least one photo-product. This reaction can be a photo-decomposition reaction, such as oxidation, reduction, or bond breaking to form smaller constituents, or a molecular rearrangement, such as a sigmatropic rearrangement, or addition reactions including pericyclic cycloadditions. Thus in an embodiment, data storage in the form of holograms is achieved wherein the photo-product is patterned (for example, in a graded fashion) within the modified optically transparent substrate to provide the at least one optically readable datum.

[0031] The photochemically active dye (hereinafter sometimes referred to as "dye") is selected and utilized on the basis of several characteristics, including the ability to change the refractive index of the dye upon exposure to light; the efficiency with which the light creates the refractive index change; and the separation between the wavelength at which the dye shows an maximum absorption and the desired wavelength or wavelengths to be used for storing and/or reading the data. The choice of the photochemically active dye depends upon many factors, such as sensitivity (S) of the holographic storage media, concentration ( $N_0$ ) of the photochemically active dye, the dye's absorption cross section ( $\sigma$ ) at the recording wavelength, the quantum efficiency (QE) of the photochemical conversion of the dye, and the refractive index change per unit dye density (i.e.,  $\Delta n/N_0$ ). Of these factors, QE,  $\Delta n/N_0$ , and  $\sigma$  are more important factors which affect the sensitivity (S) and also information storage capacity (M/#). Preferred photochemically active dyes are those that show a high refractive index change per unit dye density ( $\Delta n/N_0$ ) (as explained previously), a high quantum efficiency in the photochemical conversion step, and a low absorption cross-section at the wavelength of the electromagnetic radiation used for the photochemical conversion.

[0032] The photochemically active dye is one that is capable of being written and read by electromagnetic radiation. It is desirable to use dyes that can be written (with a signal beam) and read (with a read beam) using actinic radiation i.e., radiation having a wavelength from about 300 nm to about 1,100 nm. The wavelengths at which writing and reading are accomplished are about 300 nm to about 800 nm. In one embodiment, the writing and reading are accomplished at a wavelength of about 400 nm to about 600 nm. In another embodiment, the writing and reading are accomplished at a wavelength of about 400 to about 550 nanometers. In still another embodiment, the reading wavelength is such that it is shifted by 0 nm to about 400 nm from the writing wavelength. Exemplary wavelengths at which writing and reading are accomplished are about 405 nanometers and about 532 nanometers. In an embodiment, the photochemically active dye is a vicinal diarylethene. In another embodiment, the photochemically active dye is a photo-product derived from a vicinal diarylethene. In still another embodiment, the photochemically active dye is a nitrone. In still yet another embodiment, the photochemically active dye is a nitrostilbene. Any combination comprising two or more members selected from the group consisting of a vicinal diarylethene, a nitrone, a photo-product derived from a vicinal diarylethene, and a nitrostilbene can also be used.

[0033] An exemplary class of vicinal diarylethene compounds can be represented by generic structure (I),

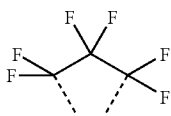
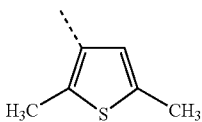
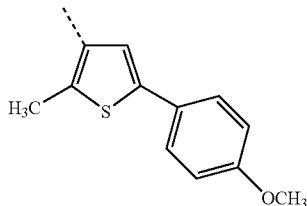
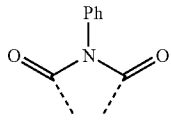
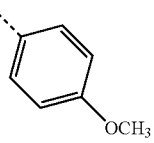
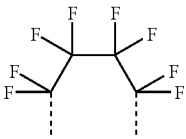
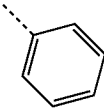


(I)

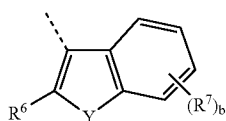
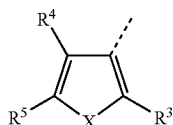
[0034] wherein “e” is 0 or 1; R¹ is a bond, an oxygen atom, a substituted nitrogen atom, a sulfur atom, a selenium atom, a divalent C₁-C₂₀ aliphatic radical, a halogenated divalent C₁-C₂₀ aliphatic radical, a divalent C₃-C₂₀ cycloaliphatic radical, a halogenated divalent C₁-C₂₀ cycloaliphatic radical, or a divalent C₂-C₃₀ aromatic radical; Ar¹ and Ar² are each independently a C₂-C₄₀ aromatic radical, or a C₂-C₄₀ heteroaromatic radical; and Z¹ and Z² are independently a bond, a hydrogen atom, a monovalent C₁-C₂₀ aliphatic radical, divalent C₁-C₂₀ aliphatic radical, a monovalent C₃-C₂₀ cycloaliphatic radical, a divalent C₃-C₂₀ cycloaliphatic radical, a monovalent C₂-C₃₀ aromatic radical, or a divalent C₂-C₃₀ aromatic radical. The Table below illustrates individual vicinal diarylethene compounds encompassed by the chemical genus represented by formula I. It should be noted that in the exemplary structures listed in the table each of the aromatic radicals Ar¹ and Ar² are identical as are the groups Z¹ and Z². It will be understood by those skilled in the art that Ar¹ may differ in structure from Ar² and that Z¹ may differ in structure from Z², and that such species are encompassed within generic structure I and are included within the scope of the instant invention.

Example	R¹	“e”	Ar¹ & Ar²	Z¹ & Z²
I-1		1		bond
I-2		1		bond
I-3		1		bond

-continued

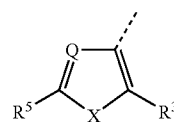
Example	R <sup>1</sup>	"e"	Ar <sup>1</sup> & Ar <sup>2</sup>	Z <sup>1</sup> & Z <sup>2</sup>
I-4		1		bond
I-5	—	0		CF <sub>3</sub>
I-6		1		bond
I-7		1		bond

[0035] In another embodiment, e is 0, and Z<sup>1</sup> and Z<sup>2</sup> C<sub>1</sub>-C<sub>5</sub> alkyl, C<sub>1</sub>-C<sub>5</sub> perfluoroalkyl, or CN. In still another embodiment, e is 1, and Z<sup>1</sup> and Z<sup>2</sup> are independently CH<sub>2</sub>, CF<sub>2</sub>, or C=O. In yet another embodiment, Ar<sup>1</sup> and Ar<sup>2</sup> are each independently an aromatic radical selected from the group consisting of phenyl, anthracenyl, phenanthrenyl, pyridinyl, pyridazinyl, 1H-phenalenyl and naphthyl, optionally substituted by one or more substituents, wherein the substituents are each independently C<sub>1</sub>-C<sub>3</sub> alkyl, C<sub>1</sub>-C<sub>3</sub> perfluoroalkyl, C<sub>1</sub>-C<sub>3</sub> alkoxy, or fluorine. In yet another embodiment at least one of Ar<sup>1</sup> and Ar<sup>2</sup> comprises one or more aromatic moieties selected from the group consisting of structures (II), (III), and (IV),



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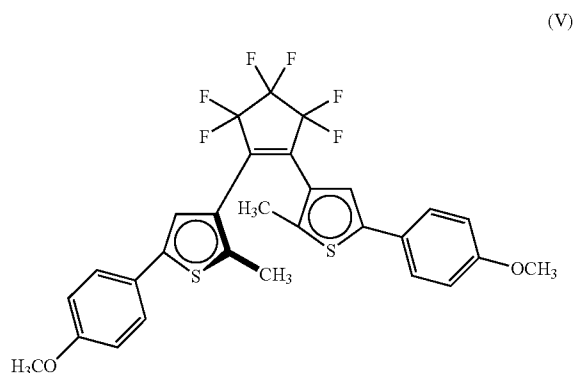
(IV)



wherein R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> are hydrogen, a halogen atom, a nitro group, a cyano group, a C<sub>1</sub>-C<sub>10</sub> aliphatic radical, a C<sub>3</sub>-C<sub>10</sub> cycloaliphatic radical, or a C<sub>2</sub>-C<sub>10</sub> aromatic radical; R<sup>7</sup> is independently at each occurrence a halogen atom, a nitro group, a cyano group, a C<sub>1</sub>-C<sub>10</sub> aliphatic radical, a C<sub>3</sub>-C<sub>10</sub> cycloaliphatic radical, or a C<sub>2</sub>-C<sub>10</sub> aromatic radical; "b" is an integer from and including 0 to and including 4; X and Y are selected from the group consisting of sulfur, selenium, oxygen, NH, and nitrogen substituted by a C<sub>1</sub>-C<sub>10</sub> aliphatic radical, a C<sub>3</sub>-C<sub>10</sub> cycloaliphatic radical, or a C<sub>2</sub>-C<sub>10</sub> aromatic radical; and Q is CH or N. In one embodiment, at least one of R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> is selected from the group consisting of hydrogen, fluorine, chlorine, bromine, C<sub>1</sub>-C<sub>3</sub> alkyl, C<sub>1</sub>-C<sub>3</sub> perfluoroalkyl, cyano, phenyl, pyridyl, isoxazolyl, —CHC(CN)<sub>2</sub>.

[0036] As mentioned previously, preferred photochemically active dyes are those that show a high refractive index change, a high quantum efficiency in the photochemical conversion step, and a low absorption cross-section at the wavelength of the electromagnetic radiation used for the photochemical conversion. One such example of a suitable photochemically active dye is illustrated by the vicinal diarylethene (V),

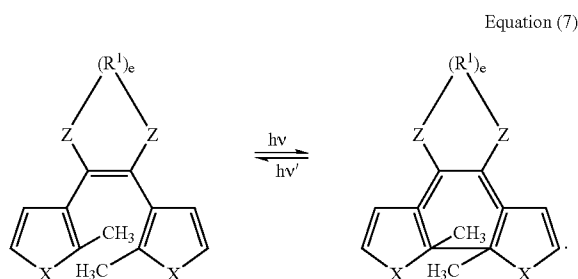




which can be named as 1,2-bis{2-(4-methoxyphenyl)-5-methylthien-4-yl}-3,3,4,4,5,5-hexafluorocyclopent-1-ene. Compound (V) shows a UV absorbance of about 1 at about 600 nanometers, the wavelength at which it cyclizes intramolecularly, and a high QE of about 0.8 for the cyclization step. Vicinal diarylethene (V) is also represented in the Table above as Example I-1 wherein, with reference to generic structure I,  $R^1$  is a perfluorotrimethylene group, “e” is 1,  $Z^1$  and  $Z^2$  are each bonds, and  $Ar^1$  and  $Ar^2$  are each 2-(4-methoxyphenyl)-5-methylthien-4-yl moieties.

[0037] Other examples of suitable vicinal diarylethenes that can be used as photochemically active dyes include diarylperfluorocyclopentenenes, diarylmaleic anhydrides, diarylmaleimides, or a combination comprising at least one of the foregoing diarylethenes. The vicinal diarylethenes can be prepared using methods known in the art.

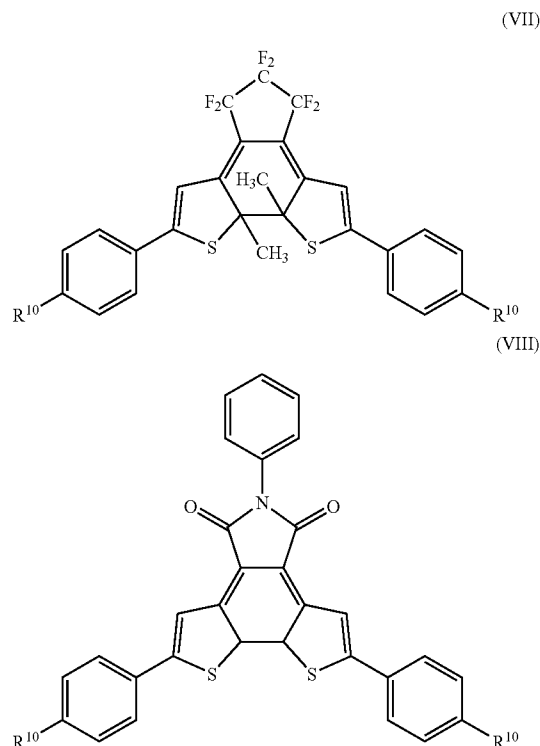
[0038] The vicinal diarylethenes can be reacted in the presence of actinic radiation (i.e. radiation that can produce a photochemical reaction), such as light. In one embodiment, an exemplary vicinal diarylethene can undergo a reversible cyclization reaction in the presence of light (hv) according to the following equation (7),



where X, Z  $R^1$  and e have the meanings indicated above. The cyclization reactions can be used to produce holograms. The holograms can be produced by using radiation to effect the cyclization reaction or the reverse ring-opening reaction. Thus, in an embodiment, a photo-product derived from a vicinal diarylethene can be used as a photochemically active dye. Such photo-products derived from the vicinal diarylethene can be represented by a formula (VI),

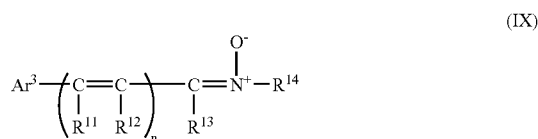


wherein “e”,  $R^1$ ,  $Z^1$ , and  $Z^2$  are as described for the vicinal diarylethene having formula (I), A and B are fused rings, and  $R^8$  and  $R^9$  are each independently a hydrogen atom, an aliphatic radical, a cycloaliphatic radical, or an aromatic radical. One or both fused rings A and B may comprise carbocyclic rings which do not have heteroatoms. In another embodiment, the fused rings A and B may comprise one or more heteroatoms selected from the group consisting of oxygen, nitrogen, and sulfur. Non-limiting examples of compounds falling within the scope of formula (VI) include the compounds (VII) and (VIII)

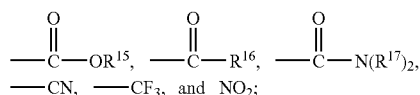


wherein  $R^{10}$  is independently at each occurrence a hydrogen atom, a methoxy radical, or a trifluoromethyl radical.

[0039] Nitrones can also be used as photochemically active dyes for producing the holographic data storage media. An exemplary nitron generally comprises an aryl nitron structure represented by the structure (IX),



wherein  $\text{Ar}^3$  is an aromatic radical, each of  $\text{R}^{11}$ ,  $\text{R}^{12}$ , and  $\text{R}^{13}$  is a hydrogen atom, an aliphatic radical, a cycloaliphatic radical, or an aromatic radical;  $\text{R}^{14}$  is an aliphatic radical (for example, an isopropyl) or an aromatic radical, and "n" is an integer having a value of from 0 to 4. In an embodiment, the radical  $\text{R}^{14}$  comprises one or more electron withdrawing substituents selected from the group consisting of



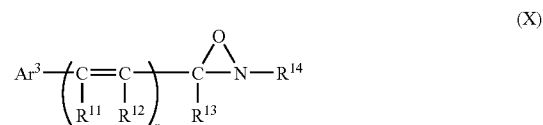
wherein  $\text{R}^{15}$ - $\text{R}^{17}$  are independently a  $\text{C}_1$ - $\text{C}_{10}$  aliphatic radical, a  $\text{C}_3$ - $\text{C}_{10}$  cycloaliphatic radical, or a  $\text{C}_2$ - $\text{C}_{10}$  aromatic radical.

[0040] As can be seen from structure (IX), the nitrones may be  $\alpha$ -aryl-N-arylnitrones or conjugated analogs thereof in which the conjugation is between the aryl group and an  $\alpha$ -carbon atom. The  $\alpha$ -aryl group is frequently substituted, often by a dialkylamino group, in which the alkyl groups contain 1 to about 4 carbon atoms. Suitable, non-limiting examples of nitrones include  $\alpha$ -(4-diethylaminophenyl)-N-phenylnitron;  $\alpha$ -(4-diethylaminophenyl)-N-(4-chlorophenyl)-nitron,  $\alpha$ -(4-diethylaminophenyl)-N-(3,4-dichlorophenyl)-nitron,  $\alpha$ -(4-diethylaminophenyl)-N-(4-carbethoxyphenyl)-nitron,  $\alpha$ -(4-diethylaminophenyl)-N-(4-acetylphenyl)-nitron,  $\alpha$ -(4-dimethylaminophenyl)-N-(4-cyanophenyl)-nitron,  $\alpha$ -(4-methoxyphenyl)-N-(4-cyanophenyl)nitron,  $\alpha$ -(9-julolidinyl)-N-phenylnitron,  $\alpha$ -(9-julolidinyl)-N-(4-chlorophenyl)nitron,  $\alpha$ -(4-Dimethylamino)styryl-N-phenyl Nitron,  $\alpha$ -Styryl-N-phenyl nitron,  $\alpha$ -[2-(1,1-diphenylethenyl)]-N-phenylnitron,  $\alpha$ -[2-(1-phenylpropenyl)]-N-phenylnitron, or a combination comprising at least one of the foregoing nitrones.

[0041] In another embodiment, the photochemically active dye is a nitrostilbene compound. Nitrostilbene compounds are illustrated by 4-dimethylamino-2',4'-dinitrostilbene, 4-dimethylamino-4'-cyano-2'-nitrostilbene, 4-hydroxy-2',4'-dinitrostilbene, and the like. The nitrostilbene can be a cis isomer, a trans isomer, or mixtures of the cis and trans isomers. Thus, in another embodiment, the photochemically active dye useful for producing a holographic data storage medium comprises at least one member selected from the group consisting of 4-dimethylamino-2',4'-dinitrostilbene, 4-dimethylamino-4'-cyano-2'-nitrostilbene, 4-hydroxy-2',4'-dinitrostilbene, 4-methoxy-2',4'-dinitrostilbene,  $\alpha$ -(4-diethylaminophenyl)-N-phenylnitron;  $\alpha$ -(4-diethylaminophenyl)-N-(4-chlorophenyl)-nitron,  $\alpha$ -(4-diethylaminophenyl)-N-(3,4-dichlorophenyl)-nitron,  $\alpha$ -(4-diethylaminophenyl)-N-(4-carbethoxyphenyl)-nitron,  $\alpha$ -(4-diethylaminophenyl)-N-(4-acetylphenyl)-nitron,

$\alpha$ -(4-dimethylaminophenyl)-N-(4-cyanophenyl)-nitron,  $\alpha$ -(4-methoxyphenyl)-N-(4-cyanophenyl)nitron,  $\alpha$ -(9-julolidinyl)-N-phenylnitron,  $\alpha$ -(9-julolidinyl)-N-(4-chlorophenyl)nitron,  $\alpha$ -[2-(1,1-diphenylethenyl)]-N-phenylnitron, and  $\alpha$ -[2-(1-phenylpropenyl)]-N-phenylnitron.

[0042] Upon exposure to electromagnetic radiation, nitrones undergo unimolecular cyclization to an oxaziridine illustrated by structure (X),



wherein  $\text{Ar}^3$ ,  $\text{R}^{11}$ - $\text{R}^{14}$ , and n have the same meaning as denoted above for the structure (IX).

[0043] The photochemically active dye is used in an amount from about 0.1 to about 10 weight percent in an embodiment, from about 1 weight percent to about 4 weight percent in another embodiment, and from about 4 weight percent to about 7 weight percent in still another embodiment, based on a total weight of the optically transparent substrate.

[0044] The optically transparent plastic materials used in producing the holographic data storage media can comprise any plastic material having sufficient optical quality, e.g., low scatter, low birefringence, and negligible losses at the wavelengths of interest, to render the data in the holographic storage material readable. Organic polymeric materials, such as for example, oligomers, polymers, dendrimers, ionomers, copolymers such as for example, block copolymers, random copolymers, graft copolymers, star block copolymers; or the like, or a combination comprising at least one of the foregoing polymers can be used. Thermoplastic polymers or thermosetting polymers can be used. Examples of suitable thermoplastic polymers include polyacrylates, polymethacrylates, polyamides, polyesters, polyolefins, polycarbonates, polystyrenes, polyesters, polyamideimides, polyarylates, polyarylsulfones, polyethersulfones, polyphenylene sulfides, polysulfones, polyimides, polyetherimides, polyetherketones, polyether etherketones, polyether ketone ketones, polysiloxanes, polyurethanes, polyarylene ethers, polyethers, polyether amides, polyether esters, or the like, or a combination comprising at least one of the foregoing thermoplastic polymers. Some more possible examples of suitable thermoplastic polymers include, but are not limited to, amorphous and semi-crystalline thermoplastic polymers and polymer blends, such as: polyvinyl chloride, linear and cyclic polyolefins, chlorinated polyethylene, polypropylene, and the like; hydrogenated polysulfones, ABS resins, hydrogenated polystyrenes, syndiotactic and atactic polystyrenes, polycyclohexyl ethylene, styrene-acrylonitrile copolymer, styrene-maleic anhydride copolymer, and the like; polybutadiene, polymethylmethacrylate (PMMA), methyl methacrylate-polyimide copolymers; polyacrylonitrile, polyacetals, polyphenylene ethers, including, but not limited to, those derived from 2,6-dimethylphenol and copolymers with 2,3,6-trimethylphenol, and the like; ethylene-vinyl acetate copolymers, polyvinyl acetate, ethylene-tetrafluoroethylene copolymer,

aromatic polyesters, polyvinyl fluoride, polyvinylidene fluoride, and polyvinylidene chloride.

[0045] In some embodiments, the thermoplastic polymer used in the methods disclosed herein as a substrate is made of a polycarbonate. The polycarbonate may be an aromatic polycarbonate, an aliphatic polycarbonate, or a polycarbonate comprising both aromatic and aliphatic structural units.

[0046] As used herein, the term “polycarbonate” includes compositions having structural units of the structure (XI),

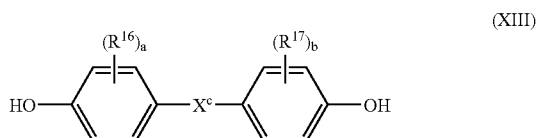


where  $\text{R}^{15}$  is an aliphatic, aromatic or a cycloaliphatic radical. In an embodiment, the polycarbonate comprises structural units of the structure (XII):



wherein each of  $\text{A}^1$  and  $\text{A}^2$  is a monocyclic divalent aryl radical and  $\text{Y}^1$  is a bridging radical having zero, one, or two atoms which separate  $\text{A}^1$  from  $\text{A}^2$ . In an exemplary embodiment, one atom separates  $\text{A}^1$  from  $\text{A}^2$ . Illustrative, non-limiting examples of radicals of this type are  $\text{---O---}$ ,  $\text{---S---}$ ,  $\text{---S(O)---}$ ,  $\text{---S(O)}_2\text{---}$ ,  $\text{---C(O)---}$ , methylene, cyclohexylmethylene, 2-ethylidene, isopropylidene, neopentylidene, cyclohexylidene, cyclopentadecylidene, cyclododecylidene, adamantylidene, and the like. Some examples of such bisphenol compounds are bis(hydroxyaryl)ethers such as 4,4'-dihydroxy diphenylether, 4,4'-dihydroxy-3,3'-dimethylphenyl ether, or the like; bis(hydroxy diaryl)sulfides, such as 4,4'-dihydroxy diphenyl sulfide, 4,4'-dihydroxy-3,3'-dimethyl diphenyl sulfide, or the like; bis(hydroxy diaryl) sulfoxides, such as, 4,4'-dihydroxy diphenyl sulfoxides, 4,4'-dihydroxy-3,3'-dimethyl diphenyl sulfoxides, or the like; bis(hydroxy diaryl)sulfones, such as 4,4'-dihydroxy diphenyl sulfone, 4,4'-dihydroxy-3,3'-dimethyl diphenyl sulfone, or the like; or combinations comprising at least one of the foregoing bisphenol compounds. In another embodiment, zero atoms separate  $\text{A}^1$  from  $\text{A}^2$ , with an illustrative example being biphenol. The bridging radical  $\text{Y}^1$  can be a hydrocarbon group, such as, for example, methylene, cyclohexylidene or isopropylidene, or aryl bridging groups.

[0047] Any of the dihydroxy aromatic compounds known in the art can be used to make the polycarbonates. Examples of dihydroxy aromatic compounds include, for example, compounds having general structure (XIII),



wherein  $\text{R}^{16}$  and  $\text{R}^{17}$  each independently represent a halogen atom, or a aliphatic, aromatic, or a cycloaliphatic radical; a and b are each independently integers from 0 to 4; and  $\text{X}^c$  represents one of the groups of structure (XIV),



wherein  $\text{R}^{18}$  and  $\text{R}^{19}$  each independently represent a hydrogen atom or a aliphatic, aromatic or a cycloaliphatic radical; and  $\text{R}^{20}$  is a divalent hydrocarbon group. Some illustrative, non-limiting examples of suitable dihydroxy aromatic compounds include dihydric phenols and the dihydroxy-substituted aromatic hydrocarbons such as those disclosed by name or structure (generic or specific) in U.S. Pat. No. 4,217,438. Polycarbonates comprising structural units derived from bisphenol A are preferred since they are relatively inexpensive and commercially readily available. A nonexclusive list of specific examples of the types of bisphenol compounds that may be represented by structure (XIII) includes the following: 1,1-bis(4-hydroxyphenyl) methane; 1,1-bis(4-hydroxyphenyl) ethane; 2,2-bis(4-hydroxyphenyl) propane (hereinafter “bisphenol A” or “BPA”); 2,2-bis(4-hydroxyphenyl) butane; 2,2-bis(4-hydroxyphenyl) octane; 1,1-bis(4-hydroxyphenyl) propane; 1,1-bis(4-hydroxyphenyl) n-butane; bis(4-hydroxyphenyl) phenylmethane; 2,2-bis(4-hydroxy-3-methylphenyl) propane (hereinafter “DMBPA”); 1,1-bis(4-hydroxy-t-butylphenyl) propane; bis(hydroxyaryl) alkanes such as 2,2-bis(4-hydroxy-3-bromophenyl) propane; 1,1-bis(4-hydroxyphenyl) cyclopentane; 9,9'-bis(4-hydroxyphenyl) fluorene; 9,9'-bis(4-hydroxy-3-methylphenyl) fluorene; 4,4'-biphenol; and bis(hydroxyaryl) cycloalkanes such as 1,1-bis(4-hydroxyphenyl) cyclohexane and 1,1-bis(4-hydroxy-3-methylphenyl)cyclohexane (hereinafter “DMBPC”); and the like, as well as combinations comprising at least one of the foregoing bisphenol compound.

[0048] Polycarbonates can be produced by any of the methods known in the art. Branched polycarbonates are also useful, as well as blends of linear polycarbonates and branched polycarbonates. Preferred polycarbonates are based on bisphenol A. Preferably, the weight average molecular weight of the polycarbonate is about 5,000 to about 100,000 atomic mass units, more preferably about 10,000 to about 65,000 atomic mass units, and most preferably about 15,000 to about 35,000 atomic mass units. Other specific examples of a suitable thermoplastic polymer for use in forming the holographic data storage media include Lexan®, a polycarbonate; and Ultem®, an amorphous polyetherimide, both of which are commercially available from General Electric Company.

[0049] Examples of useful thermosetting polymers include those selected from the group consisting of an epoxy, a phenolic, a polysiloxane, a polyester, a polyurethane, a polyamide, a polyacrylate, a polymethacrylate, or a combination comprising at least one of the foregoing thermosetting polymers.

[0050] The photochemically active dye may be admixed with other additives to form a photo-active material. Examples of such additives include heat stabilizers; antioxidants; light stabilizers; plasticizers; antistatic agents; mold releasing agents; additional resins; binders, blowing agents;

and the like, as well as combinations of the foregoing additives. The photo-active materials are used for manufacturing holographic data storage media.

[0051] Cycloaliphatic and aromatic polyesters can be used as binders for preparing the photo-active material. These are suitable for use with thermoplastic polymers, such as polycarbonates, to form the optically transparent substrate. These polyesters are optically transparent, and have improved weatherability, low water absorption and good melt compatibility with the polycarbonate matrix. Cycloaliphatic polyesters are generally prepared by reaction of a diol with a dibasic acid or an acid derivative, often in the presence of a suitable catalyst.

[0052] Generally, the polymers used for forming the optically transparent substrate, and the holographic data storage medium should be capable of withstanding the processing parameters, such as for example during the step of including the dye and application of any coating or subsequent layers and molding into final format; and subsequent storage conditions. Suitable thermoplastic polymers have glass transition temperatures of about 100° C. or greater in an embodiment, about 150° C. or greater in another embodiment, and about 200° C. or greater in still another embodiment. Exemplary thermoplastic polymers having glass transition temperatures of 200° C. or greater include certain types of polyetherimides, polyimides, and combinations comprising at least one of the foregoing.

[0053] As noted above, the effective photochemically active dye is present in an amount from about 0.1 to about 10 weight percent, based on the total weight of the optically transparent substrate, and has a UV-visible absorbance in a range between about 0.1 and about 1 at a wavelength in a range between about 300 nm and about 800 nm. Such photochemically active dyes are used in combination with other materials, such as, for example, binders to form photo-active materials, which in turn are used for manufacturing holographic data storage media. In an embodiment, a film of an optically transparent substrate comprising at least one optically transparent plastic material and at least one photochemically active dye is formed. Generally, the film is prepared by molding techniques by using a molding composition that is obtained by mixing the dye with an optically transparent plastic material. Mixing can be conducted in machines such as a single or multiple screw extruder, a Buss kneader, a Henschel, a helicone, an Eirich mixer, a Ross mixer, a Banbury, a roll mill, molding machines such as injection molding machines, vacuum forming machines, blow molding machine, or then like, or a combination comprising at least one of the foregoing machines. Alternatively, the dye and the optically transparent plastic material may be dissolved in a solution and films of the optically transparent substrate can be spin cast from the solution.

[0054] After the mixing step, the data storage composition is injection molded into an article that can be used for producing holographic data storage media. The injection-molded article can have any geometry. Examples of suitable geometries include circular discs, square shaped plates, polygonal shapes, or the like. The thickness of the articles can vary, from being at least 100 micrometers in an embodiment, and at least 250 micrometers in another embodiment. Thickness of at least 250 micrometers is useful in producing holographic data storage disks which are comparable to the thickness of current digital storage discs.

[0055] The molded data storage medium thus produced can be used for producing data storage articles, which can be used for storing data in the form of holograms. The data storage medium in the data storage article is irradiated with electromagnetic energy having a first wavelength to form a modified optically transparent substrate comprising at least one optically readable datum and at least one photo-product of the photochemically active dye. The resulting holographic data storage medium has the photo-product patterned within the optically transparent substrate to provide at least one optically readable datum. In one embodiment, the irradiation facilitates a partial chemical conversion (also sometimes referred to as "reaction") of the photochemically active dye to a photo-product, for example, the cyclization reaction of the vicinal diarylethene to a cyclized product, or the ring opening reaction of the cyclized product to the vicinal diarylethene product, or conversion of an aryl nitrone to an aryl oxaziridine product; or a decomposition product derived from the oxaziridine, thereby creating a hologram of the at least one optically readable datum.

[0056] Reading of the stored holographic data can be achieved by a read beam, which comprises irradiating the data storage medium with electromagnetic energy. The read beam reads the data contained by diffracted light from the hologram. In an embodiment, the read wavelength can be between 350 and 1,100 nanometers (nm). In one embodiment, the wavelengths of the data beam used for writing the data as holograms and the read beam used for reading the stored data are the same. In another embodiment, the wavelengths of the data beam and the read beam are different from each other, and can independently have a wavelength between 350 and 1,100 nanometers. In still another embodiment, the read beam has a wavelength that is shifted by 0 nm to about 400 nm from the wavelength of the write beam.

[0057] The methods disclosed herein can be used for producing holographic data storage media that can be used for bit-wise type data storage in an embodiment, and page-wise type storage of data in another embodiment. In still another embodiment, the methods can be used for storing data in multiple layers of the data storage medium.

[0058] The holographic data storage articles described hereinabove are useful for recording data in the form of holograms and reading the holographic data. The holographic data storage medium in the in the holographic data storage article is irradiated with electromagnetic energy having a first wavelength (the signal beam or the write beam) having data to be written. This leads to the formation of a modified optically transparent substrate comprising at least one photo-product of the at least one photochemically active dye (described previously), and at least one optically readable datum. The data is then stored in the data storage medium as a hologram. Then the holographic data storage medium is irradiated with electromagnetic energy having a second wavelength (the read beam) to read the hologram. In an embodiment, the read beam has a wavelength that is shifted by 0 nanometer to about 400 nanometers from the signal beam's wavelength.

[0059] While the disclosure has been illustrated and described in typical embodiments, it is not intended to be limited to the details shown, since various modifications and substitutions can be made without departing in any way from the spirit of the present disclosure. As such, further

modifications and equivalents of the disclosure herein disclosed may occur to persons skilled in the art using no more than routine experimentation, and all such modifications and equivalents are believed to be within the spirit and scope of the disclosure as defined by the following claims.

## EXAMPLES

### Example 1

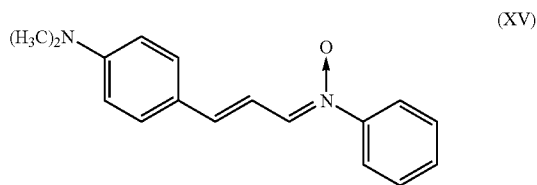
#### Preparation of 4'-methoxy-2,4-dinitrostilbene

[0060] To a 2 liter 3-necked round-bottomed flask equipped with a condenser, a Dean-Stark trap, a mechanical stirrer, nitrogen inlet, heating mantle, thermometer, and a Therm-o-watch® temperature controller, was added p-anisaldehyde (149.8 grams, 1.1 moles), 2,4-dinitrotoluene (182 grams, 1.0 mole), xylene (500 milliliters), and piperidine (50 milliliters, 0.5 mole). The resulting mixture was heated with the temperature on the Therm-o-watch® temperature controller set at 145° C. After stirring and heating for about 2 hours, approximately 20 milliliters of water had collected in the Dean-Stark trap. The reaction solution was allowed to cool to room temperature, and then further cooled with an ice water bath for an additional hour during which time the desired product crystallized from the solution. The solid material was filtered, rinsed with pentane, and dried in a vacuum oven at 100° C. for 12 hours to give 257.1 grams (85.6 percent of theory) of the desired product as a dark red crystalline solid.

### Example 2

#### Preparation of $\alpha$ -(4-Dimethylamino)styryl-N-phenyl nitrone

[0061] To a 1-liter, 3-necked round-bottomed flask equipped with a mechanical stirrer and a nitrogen inlet was added phenylhydroxyamine (27.3 grams, 0.25 mole), (4-dimethylamino)cinnamaldehyde (43.81 grams, 0.25 mole), and ethanol (250 milliliters). To the resulting bright orange slurry was added methanesulfonic acid (250 microliters) via a syringe. The bright orange slurry turned to a deep red and all solids dissolved. Within five minutes, an orange solid formed. Pentane (about 300 milliliters) was added to facilitate stirring of the reaction mixture. The solid was filtered and dried in a vacuum oven at 80° C. for several hours to give 55.9 grams (84 percent of theory) of the desired product as a bright orange solid. The dye has structure (XV):

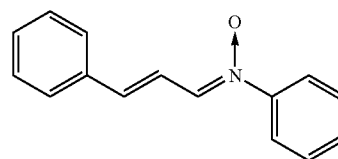


### Example 3

#### Preparation of $\alpha$ -Styryl-N-phenyl nitrone

[0062] N-Isopropylhydroxylamine hydrochloride (5.04 grams, 45.2 millimoles, 1 molar equivalent; available from

Acros Organics) was combined with trans-cinnamaldehyde (5.66 grams, 42.9 millimoles, 0.95 molar equivalent; available from Aldrich Chemical Company) in 16 milliliters of water. The rapidly stirred mixture started off as an emulsion due to the low solubility of the trans-cinnamaldehyde. After about one hour, the emulsion disappeared, and a homogeneous light yellow solution resulted. After being stirred for four hours, the reaction mixture was poured into methylene chloride and treated with 26 milliliters of saturated aqueous sodium carbonate solution (containing greater than 2 molar equivalents of sodium carbonate base to insure consumption of hydrogen chloride by-product) such that the pH was about 10.5. The phases were separated and the aqueous phase was rinsed with additional methylene chloride. The combined organic phase was separated, dried over anhydrous magnesium sulfate, concentrated in vacuo, and dried under vacuum overnight to produce 7.4 grams (91 percent of theory) of the desired product that was determined to be pure by liquid chromatography and further characterized by NMR spectroscopy. UV-visible spectrum of the product in absolute ethanol revealed an absorption maximum ( $\lambda_{max}$ ) at 330 nanometers. Exposure of this dilute solution to a 390 nanometer light source converted the nitrone to the corresponding oxaziradine with a shift of the absorption maximum to 256 nanometers. All sample manipulations were done in a dark room containing only red light to insure the stability of  $\alpha$ -styryl-N-phenyl nitrone. The dye has structure (XVI):



### Example 4

[0063] This Example describes the procedure for preparing a  $\alpha$ -(4-Dimethylamino)styryl-N-phenyl Nitrone—Polystyrene blend, which was subsequently used for preparing molded disks having a thickness of about 1.2 millimeters.

[0064] Ten kilograms of crystal polystyrene 1301 pellets (obtained from Nova Chemicals) were ground to a coarse powder in a Retsch mill and dried in a circulating air oven maintained at 80° C. for several hours. In a 10-liter Henschel mixer, 6.5 kilograms of the dry polystyrene powder and 195 grams of  $\alpha$ -(4-dimethylamino)styryl-N-phenyl nitrone were blended to form a homogeneous orange powder. The powder blend was then fed to a WP 28 millimeter twin-screw extruder at 185° C. to give 6.2 kilograms of dark orange pellets with a nominal dye content of about 3 weight percent. This material was then further diluted with additional crystal polystyrene 1301 pellets to make blends having 0.60 weight percent, 0.75 weight percent, 1 weight percent, and 1.24 weight percent of  $\alpha$ -(4-dimethylamino)styryl-N-phenyl nitrone. Each of these four diluted blend compositions was re-processed with the WP 28 millimeter twin-screw extruder to form homogeneously colored pellets.

[0065] Optical quality disks were prepared by injection molding the four diluted blends (prepared as described above) with an ELECTRA DISCO™ 50-ton all-electrical

commercial CD/DVD (compact disc/digital video disc) molding machine (available from Milacron Inc.). Mirrored stampers were used for both surfaces. Cycle times were generally set to about 10 seconds. Molding conditions were varied depending upon the glass transition temperature and melt viscosity of the polymer used, as well as the photochemically active dye's thermal stability. Thus the maximum barrel temperature was varied from about 200° C. to about 375° C.

#### Example 5

[0066] Procedures for preparing molded disks using the Mini-jector®. The molding conditions varied depending upon the nature of the polymer matrix used to incorporate the photochemically active dye. Typical conditions used for molding OQ (Optical Grade) polycarbonate and polystyrene based blends of the photochemically active dyes are shown in Table 1.

TABLE 1

Molding Parameters	OQ Polycarbonate	
	Powder	Polystyrene Powder
Barrel Temp. (Rear) (° F.)	500	400
Barrel Temp. (Front) (° F.)	540	395
Barrel Temp. (Nozzle) (° F.)	540	395
Mold Temp. (° F.)	200	100
Total Cycle Time (sec)	35	25
Switch Point (inch)	0.7	0.7
Injection Transition (inch)	0.22	0.22
Injection Boost Press. (psi)	950	850
Injection Hold Press. (psi)	300	250

#### Example 6

[0067] Procedure for measuring UV-visible spectra of the photochemically active dyes. All spectra were recorded on a Cary/Varian 300 UV-visible spectrophotometer using injection-molded disks having a thickness of about 1.2 millimeters. Spectra were recorded in the range of 300 nanometers to 800 nanometers. Due to disk-to-disk variations, no reference sample was used. Results of the UV-visible absorption spectra measurements are shown in Table 2 as Examples 7-11.

[0068] The absorption reported in the table was calculated by subtracting the average baseline in the range of 700-800 nanometers for each sample tested from the measured absorption at either 405 nanometers or 532 nanometers. Since these compounds do not absorb in the 700-800 nanometer range, this correction removed the apparent absorption caused by reflections off the surfaces of the disk and provided a more accurate representation of the absorbance of the dye. The polymers used in these examples had little or no absorption at 405 nanometers or 532 nanometers.

[0069] Examples 7-10 used  $\alpha$ -(4-Dimethylamino)styryl-N-phenyl nitrone as the photochemically active dye, and Example 11 used  $\alpha$ -styryl-N-phenyl nitrone.

TABLE 2

Example Number	Photo-chemically Active Dye Structure	Dye concentration (weight percent)	Observation Wavelength (nanometers)	Absorbance at observation wavelength	M#
7	XV	0.6	532	0.33	0.66
8	XV	0.75	532	0.42	0.86
9	XV	1	532	0.57	1.01
10	XV	1.24	532	0.7	1.28
11	XVI	2.9	405	0.58	2.5

[0070] The data in Table 2 shows that an M# of 0.5 or higher can be achieved by using from about 0.1 to about 10 weight percent of a dye, based on a total weight of the optically transparent substrate, wherein the photochemically active dye has a UV-visible absorbance in a range from about 0.1 to about 1 at a wavelength in a range from about 300 nanometers to about 800 nanometers. The results also show that high volumetric data storage capacities can be achieved using photochemically active dyes that are efficient and sensitive to electromagnetic energy, such as light without interference from the main absorption peak of the dye.

1. A method of making a holographic data storage medium, said method comprising:

- providing an optically transparent substrate comprising at least one photochemically active dye; and
- irradiating the optically transparent substrate at at least one wavelength at which the optically transparent substrate has an absorbance in a range from about 0.1 to 1, said at least one wavelength being in a range from about 300 nanometers to about 800 nanometers, to produce a modified optically transparent substrate comprising at least one optically readable datum and at least one photo-product of the photochemically active dye,

wherein the optically transparent substrate is at least 100 micrometers thick, and comprises the photochemically active dye in an amount corresponding to from about 0.1 to about 10 weight percent based on a total weight of the optically transparent substrate.

2. The method of claim 1, wherein said at least one optically readable datum comprises at least one volume element having a refractive index which is different from a corresponding volume element of the optically transparent substrate, said volume element being characterized by a change in refractive index relative to the refractive index of the corresponding volume element prior to irradiation.

3. The method of claim 1, wherein the data storage medium has a data storage capacity, as measured by M/# of greater than 0.5.

4. The method of claim 1, wherein the at least one photo-product is patterned within the modified optically transparent substrate to provide the at least one optically readable datum.

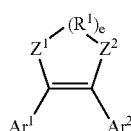
5. The method of claim 1, wherein the at least one photochemically active dye comprises a vicinal diarylethene.

6. The method of claim 1, wherein the at least one photochemically active dye comprises a nitron.

7. The method of claim 1, wherein the at least one photochemically active dye comprises a nitrostilbene.

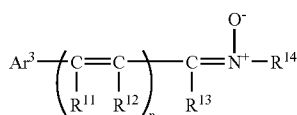
8. The method of claim 1, wherein the at least one photochemically active dye comprises a photo-product derived from a vicinal diarylethene.

9. The method of claim 5, wherein the vicinal diarylethene has the structure (I)



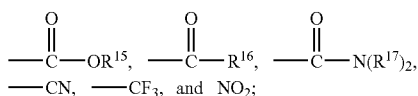
wherein “e” is 0 or 1; R¹ is a bond, an oxygen atom, a substituted nitrogen atom, a sulfur atom, a selenium atom, a divalent C₁-C₂₀ aliphatic radical, a halogenated divalent C₁-C₂₀ aliphatic radical, a divalent C₃-C₂₀ cycloaliphatic radical, a halogenated divalent C₁-C₂₀ cycloaliphatic radical, or a divalent C₂-C₃₀ aromatic radical; Ar¹ and Ar² are each independently a C₂-C₄₀ aromatic radical, or a C₂-C₄₀ heteroaromatic radical; and Z¹ and Z² are independently a bond, a hydrogen atom, a monovalent C₁-C₂₀ aliphatic radical, divalent C₁-C₂₀ aliphatic radical, a monovalent C₃-C₂₀ cycloaliphatic radical, a divalent C₃-C₂₀ cycloaliphatic radical, a monovalent C₂-C₃₀ aromatic radical, or a divalent C₂-C₃₀ aromatic radical.

10. The method of claim 6, wherein the nitrone comprises an aryl nitrone having a structure (IX):



wherein Ar³ is an aromatic radical, each of R¹¹, R¹², and R¹³ is a hydrogen atom, an aliphatic radical, a cycloaliphatic radical, or an aromatic radical; R¹⁴ is an aliphatic radical or an aromatic radical, and “n” is an integer having a value of from 0 to 4.

11. The method of claim 10, wherein R¹⁴ comprises at least one electron withdrawing substituent selected from the group consisting of



wherein R¹⁵-R¹⁷ are independently a C₁-C₁₀ aliphatic radical, a C₃-C₁₀ cycloaliphatic radical, or a C₂-C₁₀ aromatic radical.

12. The method of claim 1, wherein the at least one photochemically active dye is selected from the group consisting of 4-dimethylamino-2',4'-dinitrostilbene, 4-dimethylamino-4'-cyano-2'-nitrostilbene, 4-hydroxy-2',4'-dinitrostilbene, 4-methoxy-2',4'-dinitrostilbene, α-(4-diethylaminophenyl)-N-phenylnitron, α-(4-diethylaminophenyl)-N-(4-chlorophenyl)-nitron, α-(4-diethylaminophenyl)-N-(3,4-dichlorophenyl)-nitron, α-

diethylaminophenyl)-N-(4-carbethoxyphenyl)-nitron, α-(4-diethylaminophenyl)-N-(4-acetylphenyl)-nitron, α-(4-dimethylaminophenyl)-N-(4-cyanophenyl)-nitron, α-(4-methoxyphenyl)-N-(4-cyanophenyl)nitron, α-(9-julolidinyl)-N-phenylnitron, α-(9-julolidinyl)-N-(4-chlorophenyl)nitron, α-(4-Dimethylamino)styryl-N-phenyl Nitron, α-Styryl-N-phenyl nitron, α-[2-(1,1-diphenylethenyl)]-N-phenylnitron, α-[2-(1-phenylpropenyl)]-N-phenylnitron, and 1,2-bis{2-(4-methoxyphenyl)-5-methylthien-4-yl}-3,3,4,4,5,5-hexafluorocyclopent-1-ene.

13. The method of claim 1, wherein the optically transparent substrate comprises a thermoplastic polymer, a thermosetting polymer, or a combination of a thermoplastic polymer and a thermosetting polymer.

14. The method of claim 13, wherein the thermoplastic polymer is selected from the group consisting of polyacrylates, polymethacrylates, polyesters, polyolefins, polycarbonates, polystyrenes, polyesters, polyamides, polyamide-imides, polyarylates, polyarylsulfones, polyethersulfones, polyphenylene sulfides, polysulfones, polyimides, polyetherimides, polyetherketones, polyether etherketones, polyether ketone ketones, polysiloxanes, polyurethanes, polyethers, polyarylene ethers, polyether amides, polyether esters, or a combination comprising at least one of the foregoing thermoplastic polymers.

15. The method of claim 13, wherein the thermosetting polymer is selected from the group consisting of an epoxy thermosetting polymer, a phenolic thermosetting polymer, a polysiloxane thermosetting polymer, a polyester thermosetting polymer, a polyurethane thermosetting polymer, a polyamide thermosetting polymer, a polyacrylate thermosetting polymer, a polymethacrylate thermosetting polymer, or a combination comprising at least one of the foregoing thermosetting polymers.

16. The method of claim 13, wherein the thermoplastic polymer comprises a polycarbonate comprising structural units derived from bisphenol A.

17. The method of claim 1, wherein the at least one photo-product comprises a photo-decomposition product of the at least one photochemically active dye.

18. The method of claim 1, wherein the at least one photo-product comprises a molecular rearrangement product of the at least one photochemically active dye.

19. An optical writing and reading method, comprising:

irradiating a holographic data storage medium with a signal beam possessing data and a reference beam simultaneously to partly convert the photochemically active dye into at least one photo-product and store the data in the signal beam as a hologram in the holographic data storage medium; the holographic storage medium comprising an optically transparent substrate and at least one photochemically active dye; the optically transparent substrate having a thickness of at least 100 micrometers, and comprising the photochemically active dye in an amount corresponding to from about 0.1 to about 10 weight percent based on a total weight of the optically transparent substrate, and having a UV-visible absorbance in a range from about 0.1 to 1 at at least one wavelength in a range from about 300 nanometers to about 800 nanometers; and

irradiating the holographic storage medium with a read beam and reading the data contained by diffracted light from the hologram.

20. The method of claim 19, wherein the read beam has a wavelength that is shifted by 0 nanometers to about 400 nanometers from the signal beam's wavelength.

21. A method for using a holographic data storage article, the method comprising the steps of:

irradiating a holographic data storage medium in the holographic data storage article with electromagnetic energy having a first wavelength, the holographic data storage medium comprising an optically transparent substrate that is at least 100 micrometers thick and comprises at least one photochemically active dye in an amount corresponding to from about 0.1 to about 10 weight percent based on a total weight of the optically transparent substrate, said irradiating being done at at least one wavelength at which the optically transparent substrate has an absorbance in a range from about 0.1 to 1, and said at least one wavelength being in a range from about 300 nanometers to about 800 nanometers;

forming a modified optically transparent substrate comprising at least one photo-product of the at least one photochemically active dye, and at least one optically readable datum stored as a hologram; and

irradiating the holographic data storage medium in the article with electromagnetic energy having a second wavelength to read the hologram.

22. The method of claim 21, wherein the second wavelength is shifted by 0 nanometer to about 400 nanometers from the first wavelength.

23. The method of claim 21, wherein the first wavelength is not the same as the second wavelength.

24. The method of claim 21, wherein the first wavelength is the same as the second wavelength.

25. The method of claim 21, wherein said at least one photo-product comprises a vicinal diarylethene, a photo-product derived from the vicinal diarylethene, an oxaziridine, or a decomposition product derived from the oxaziridine.

26. A method of manufacturing a holographic data storage medium, the method comprising:

forming a film of an optically transparent substrate comprising at least one optically transparent plastic material, and at least one photochemically active dye,

wherein the optically transparent substrate is at least 100 micrometers thick; and comprises the photochemically active dye in an amount corresponding to from about 0.1 to about 10 weight percent based on a total weight of the optically transparent substrate, and has a UV-visible absorbance in a range from about 0.1 to 1 at at least one wavelength in a range from about 300 nanometers to about 800 nanometers.

27. The method of claim 26, wherein the film of the optically transparent substrate is formed by a molding technique.

28. The method of claim 26, wherein the film of the optically transparent substrate is formed by a spin casting technique.

29. The method of claim 26, wherein the at least one optically transparent plastic material comprises a thermoplastic polymer, a thermosetting polymer, or a combination of a thermoplastic polymer and a thermosetting polymer.

30. A holographic data storage medium comprising:

an optically transparent substrate comprising at least one optically transparent plastic material, at least one photochemically active dye, and at least one photo-product thereof;

said optically transparent substrate being at least 100 micrometers thick, said photochemically active dye being present in the optically transparent substrate in an amount corresponding to from about 0.1 to about 10 weight percent based on a total weight of the optically transparent substrate, said optically transparent substrate having a UV-visible absorbance in a range from about 0.1 to 1 at at least one wavelength in a range from about 300 nanometers to about 800 nanometers; and said at least one photo-product being patterned within the optically transparent substrate to provide at least one optically readable datum comprised within the holographic storage medium.

31. The holographic data storage medium of claim 30, wherein the at least one photo-product results from a photochemical conversion of the at least one photochemically active dye during the storage of data as a hologram.

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