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(71) Applicants and

(72) Inventors: **PETROV, Michael, P.** [RU/RU]; 35 Morise
Torez Av., Bldg 1, Apt. 16, St.Petersburg, 194223 (RU).
PETROV, Victor, M. [RU/RU]; 9 Peredovicov St., Apt.
128, St.Petersburg (RU).

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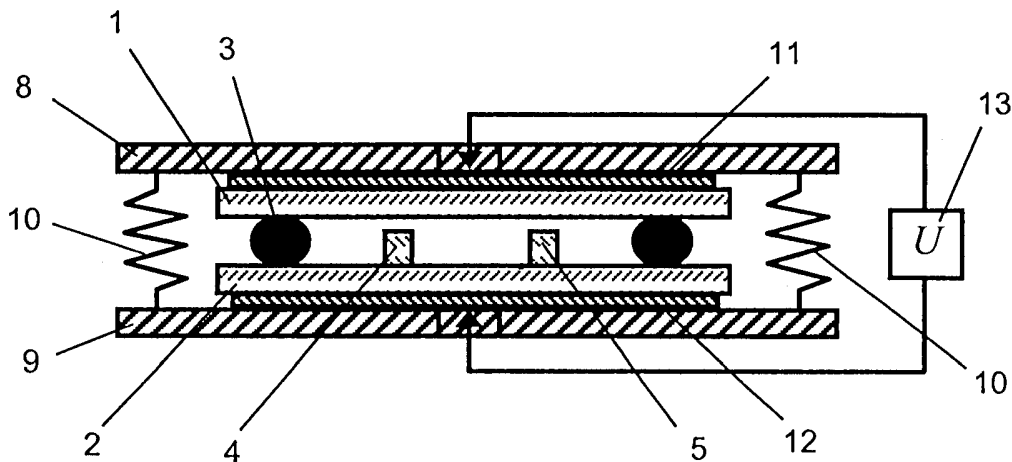
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(54) Title: ELECTROOPTICAL PHOTOSENSITIVE POLYMER MATERIAL



(57) Abstract: New electrooptical photosensitive polymer material is obtained as a result of prepolymerization of methylmethacrylate. The material contains poly , methylmethacrylate; unreacted methylmethacrylate monomer; electrooptical chromophore, the chromophore molecules having preferentially the same polar orientation; and one or several photoinitiators, which are sensitive in different spectral ranges. The proposed material simultaneously possesses both electrooptical and photosensitive properties and can be used for fabrication of optical devices, including electrically controlled ones.



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ELECTROOPTICAL PHOTSENSITIVE POLYMER MATERIAL

FIELD OF THE INVENTION

5 The present invention relates to high-molecular compounds, more particularly, to polymer materials that possess both electrooptical and photosensitive properties and can be used for fabrication of various optical devices.

BACKGROUND OF THE INVENTION

10 One of the major requirements for the optical materials to be used in the devices designed for multiplexing and demultiplexing of optical signals, in particular, optical spectral filters, is that they should exhibit photosensitive and electrooptical properties. Photosensitivity of the material enables recording of holograms, which are typically diffraction gratings, while its electrooptical properties are used for fabrication of
15 electrically controlled optical devices.

 Polymers with photorefractive properties are known and used for recording of holograms, in particular, holographic diffraction gratings, to be a component of optical filters and devices designed for multiplexing of optical signals. A typical composition of such a polymer and includes 42 % of poly-N-vinylcarbazole as the so-called polymer
20 matrix, 7 % of N-ethylcarbazole as a plasticizer, 25 % of 2,5-dimethyl-4,4'-nitrophenylazoanisole as a nonlinear chromophore, 25 % of 3-methoxy-4,4'-nitrophenylazoanisole as as a nonlinear chromophore, and 1 % of 2,4,7-trinitrofluorenone as a TNF sensitizer. The polymer sample is prepared in the form of a thin layer sandwiched between two transparent electrodes deposited on glass plates. The
25 sample thickness ranges from several tens to one-two hundred of microns. For instance, in [1] the sample thickness was 125 μm . Photosensitivity of such polymers is provided by a sensitizer. For instance, some polymers had sensitivity in the red region of the spectrum (in the vicinity of 633 nm). Photoconductivity of the polymer was provided by poly-N-vinylcarbazole, and the electrooptical properties resulted from nonlinear
30 chromophore. An external electric field with a strength of the order of $6.2 \cdot 10^7$ V/m was

applied to the sample to ensure transfer of photoinduced charges during hologram recording.

One of important shortcomings of photorefractive polymers is high light absorption and scattering. Because of this, they can be used only as thin samples with the thickness of not more than 0.2 mm. Taking into account that 1 cm sample thickness is required for achieving spectral selectivity of the order of 10^{-5} with a filter based on Bragg diffraction, it becomes evident that photorefractive polymers are unsuitable for the applications where high spectral selectivity is needed.

Another shortcoming of photorefractive polymers is the necessity for application of a very high external electric field both during hologram recording and readout. The hologram exists in the photorefractive polymer only when it is illuminated with recording radiation and when an external electric field with the strength of about $6.2 \cdot 10^7$ V/m is applied to the sample. This means that a 1 cm thick sample requires application of an electric field of about 620 kV, which is technically unfeasible.

There are polymers exhibiting photosensitive properties, i.e., photosensitive polymers, which are used for hologram recording.

In particular, a polymer including polymethylmethacrylate (PMMA) as a matrix and titanocene dichloride as a photoinitiator. The described polymer is prepared as follows. A high-purity monomer of methylmethacrylate (MMA) in a liquid form is mixed with a photoinitiator and thermoinitiator (2,2'-azobis-2-methylpropionite in the ratio 98:1:1). The obtained mixture is placed into a cuvette in the form of two parallel glass plates with an elastic polychlorvinyl ring between them. The mixture fills the cavity formed by the inner space of the ring confined by the plates. The cuvette with the mixture is placed into a heating chamber and kept there for 48 hours at 50°C. As a result of the prepolymerization reaction initiated by the thermoinitiator, the samples becomes solid after this period of time; about 90 % of the monomer becomes a polymer - polymethylmethacrylate, and the remaining 10 % of the monomer remain in the sample in the form of a free monomer - methylmethacrylate. A specific feature of the reaction is that a part of the initial monomer of methylmethacrylate remains unpolymerized. For this reason this process is called prepolymerization. The free methylmethacrylate monomer

and the photoinitiator contained into the composition of the obtained polymer provide its photosensitive properties, which manifest themselves as follows.

When a diffraction grating is recorded by, for example, two intersecting coherent light beams, an interference pattern is formed in the sample. The wavelength of recording light has to match the absorption spectrum of the photoinitiator. For example, if titanocene dichloride mentioned above is used as a photoinitiator, the recording light wavelength has to be chosen in the green region of the spectrum. When the sample is exposed to the light, the photochemical reaction starts. A molecule of the photoinitiator decays into two radicals, which initiate polymerization of free molecules of the methylmethacrylate monomer thus forming macroradicals, i.e., very long molecules. As a result, a local variation in the density of the material arises in the illuminated regions, followed by a corresponding change in the refractive index, i.e., recording of the diffraction grating.

As opposed to photorefractive polymers, the photosensitive polymers considered above have low absorption and scattering coefficients, and therefore samples of sufficient thickness can be made. However, this material does not exhibit any electrooptical properties, which hinders their applications in electrically controlled optical devices.

When a diffraction grating is recorded by, for example, two intersecting coherent light beams, an interference pattern is formed in the sample. The recording radiation wavelength has to be matched with the absorption spectrum of the photoinitiator. For example, if titanocene dichloride mentioned above is used as a photoinitiator, the sample is sensitive in the green region of the spectrum. On exposure to light, the photochemical reaction starts. A molecule of the photoinitiator decays into two radicals, which initiate polymerization of free molecules of the methylmethacrylate monomer thus forming macroradicals, i.e., very long molecules. As a result, a local variation in the density of the material arises in the illuminated sites, which leads to a corresponding change in the refractive index, i.e., recording of the diffraction grating.

In contrast to photorefractive polymers, the photosensitive polymers considered above have low absorption and scattering coefficients, and therefore samples of

sufficient thickness can be made. However, this material does not exhibit electrooptical properties, which makes them inapplicable for electrically controlled optical devices.

There are polymers exhibiting electrooptical properties - electrooptical polymers, used, for example, for electrooptical modulation of the light wave phase. The electrooptical polymers typically contain 50-70 % of polymethylmethacrylate as a matrix, and the remaining 50-30 % are electrooptical chromophores, or nonlinear chromophores. The electrooptical chromophore can be, for instance, 2,5-dimethyl-4,4'-nitrophenylazoanisole and 3-methoxy-4,4'-nitrophenylazoanisole or ring-locked phenyltertaene bridged chromophore (CLD). Other molecules can also be used as an electrooptical chromophore provided that they are oblong and bipolar.

Electrooptical properties of such a polymer are achieved by heating it up to the poling temperature and application of an external electric field. The heating provides required mobility of the chromophore molecules, and the applied electric field orients them in a given direction. As a result, the polymer sample acquires a preferred polar axis and gains electrooptical properties. In this respect, the electrooptical polymers are analogs of electrooptical ferroelectric crystals.

As a significant drawback of the electrooptical polymers it can be noted that they cannot be used for hologram recording because of the absence of photosensitive properties.

The object of the present invention is to create a new class of polymer materials – electrooptical photosensitive polymers (EPP) possessing simultaneously both electrooptical and photosensitive properties.

SUMMARY OF THE INVENTION

According to this invention, the electrooptical photosensitive polymer material consists of electrooptical chromophore, photoinitiator, and the product of methylmethacrylate prepolymerization, that contains polymethylmethacrylate and unreacted methacrylate monomer. The above ingredients are represented in the following proportion (in wt %):

electrooptical chromophore -	10-30;
photoinitiator -	up to 1;

methacrylate prepolymerization product - the rest;
the chromophore molecules having preferentially the same polar orientation.

Since different photoinitiators and chromophores their properties in certain spectral ranges, the particular type of the photoinitiator and chromophore is chosen
5 depending on the wavelength range in which the proposed polymer material will be used.

The substance, used as the initiator, has to absorb light in the desired spectral region, decay into radicals, and thus provides the required photochemical reaction. For example, if titanocene dichloride is used as a photoinitiator, the obtained polymer has its photosensitivity in the green region. If the photoinitiator is 2,2-dimethoxy-2-
10 phenylacetophenone (DMPA), $C_{16}H_{10}O_3$, the obtained polymer will be photosensitive in the ultraviolet region in the vicinity of 351 nm.

The major requirement to the chromophore is that it has to have oblong bipolar molecules. There a number of references that give examples of such chromophores; all of them can be used to obtain the polymer of the present invention [1, 2, 10, 11]. In
15 particular, in [1, 2] 2,5-dimethyl-4,4'-nitrophenylazoanisole and 3-methoxy-4,4'-nitrophenylazoanisole are described as chromophores.

For example, if 2,5-dimethyl-4,4'-nitrophenylazoanisole is used as a chromophore, the polymer with the electrooptical properties in the red and near-infrared spectral regions can be obtained.

20 The proportion between the ingredients of the polymer material of the present invention is determined by contradictory requirements for photosensitive and electrooptical properties of the material on the one hand and high optical quality on the other hand. In order to be used for fabrication of optical devices, in particular, optical spectral filters, the proposed polymer material has to meet the above requirements
25 simultaneously.

The concentrations of the ingredients given above in the electrooptical photosensitive polymer of the present invention were experimentally found to be optimal with respect to the compromise between the acceptable light absorption and photosensitivity and electrooptical properties. The optimal ingredient proportion
30 indicated above provides the following characteristics of the polymer material:

optical absorption of a 1 cm thick sample – not more than 5 %;

photosensitivity - approximately 20 mJ/cm²;

electrooptic coefficient - approximately $(2\div 3) \cdot 10^{-12}$ m/V.

If the concentration of the photoinitiator is greater than its optimal value indicated above, the obtained material still has photosensitivity. However such polymer is practically unusable as an optical material because of high light absorption induced by higher photoinitiator concentration.

The similar situation is observed with the concentration of the chromophore, that provides electrooptical properties of the invented material. On the one hand, if the chromophore concentration is less than 10 %, the obtained material has extremely low electrooptic coefficient, which prevents from using the material for electrically control of refractive index in optical devices. On the other hand, if the chromophore concentration is higher than 30 %, the obtained material has good electrooptical properties, but strongly absorbs and scatters light, which also makes the material unusable as an optical material.

As mentioned above, the photoinitiator determines the spectral range where the invented polymer material exhibits its photosensitive properties. In order to provide photosensitivity of the invented material in several different spectral ranges simultaneously, one or more photoinitiators, that have their photosensitivity in different spectral ranges, can be added to the material composition at amount less than 1 % for each additional photoinitiator.

Thus, the present invention enables a new class of polymer materials which are electrooptical photosensitive polymers. If the material contains several photoinitiators, it has photosensitivity in multiple spectral ranges, which substantially extends its applications in fabrication of various optical devices

The electrooptical photosensitive polymer of the present invention can be fabricated as follows. The ingredients indicated above, i.e., the photoinitiator and nonlinear chromophore, are added to a high-purity monomer of methylmethacrylate, and the monomer with the added ingredients is stirred to obtain a homogeneous mixture. The obtained mixture is then placed into a special cuvette, which is constructed so that access of air to the mixture is prevented both at the stage of mixture loading into the cuvette and during prepolymerization, and kept at a temperature of about 50°C until the prepolymerization is finished. The process is carried out in the dark and under

mechanical pressure applied to the mixture. At the initial stage of the process, until the mixture begins to thicken, the mixture is stirred by, for example, periodically turning the cuvette, which prevents separation of the components of the mixture under their own weight. From the moment the mixture begins to thicken, the electric field of the range
5 $(4\div 10)\cdot 10^5$ V/m is applied. The field is kept applied until the prepolymerization is completed. The electric field provides alignment of polar molecules in one direction. As a result, the material becomes solid and acquires both the photosensitive and electrooptical properties.

When the prepolymerization process is over, the cuvette with the polymer sample
10 is cooled, the cooling rate being not more than $0.25^\circ\text{C}/\text{min}$. If cooling is more rapid, the glass or polymer can crack because of different thermal expansion coefficients of these materials.

In order to accelerate prepolymerization, a thermoinitiator is added to the mixture during its preparation. The thermoinitiator may be, for instance, 2,2'-Azobis(2-methylpropionite). The thermoinitiator determines the time of reaction. In particular,
15 if the amount of the thermoinitiator is approximately 1% of the mixture, the total time of reaction is of the order of 48 hours. If the thermoinitiator is not used, the time of reaction is of the order of 4-5 days, i.e., 2-2.5 times as long as the time of reaction in the case the amount of the thermoinitiator indicated above is used. On the other hand, the optical
20 characteristics (light absorption and scattering coefficients) of the polymer sample prepared from the initial mixture without thermoinitiator are better. By increasing the concentration of the thermoinitiator to above 1 %, the time of prepolymerization can be made even shorter, however, this adversely affects the optical characteristics of the obtained sample.

25 To prepare a polymer with high optical properties (low scattering and high homogeneity), the monomer is kept under a constant external mechanical pressure of the order of $3\text{-}5\text{ kg}/\text{cm}^2$ during the entire prepolymerization process.

BRIEF DESCRIPTION OF THE DRAWINGS

30 Fig. 1 shows the cuvette used for preparation of the polymer sample in accordance with the present invention;

Fig. 2 shows the cuvette of Fig.1 placed into a holder to provide application of the external electric field and mechanical pressure to the sample during its preparation;

Fig. 3 shows the prepared sample of the electrooptical photosensitive polymer of the present invention;

5 Fig. 4 shows the optical scheme for recording a holographic diffraction grating in the prepared sample;

Fig. 5 shows the optical scheme for readout of the holographic grating recorded in the sample to measure the grating and sample characteristics.

10 DETAILED DESCRIPTION OF THE INVENTION

The electrooptical photosensitive polymer of the present invention is fabricated in a special cuvette that is design reasoning from the following characteristics of the substances and processes used:

- in its initial state the monomer of methylmethacrylate is a readily evaporating
15 liquid substance with extremely high chemical activity;
- the prepolymerization process takes several tens of hours and requires heating of the initial polymer material;
- during the prepolymerization process the mixture of methylmethacrylate with the components indicated above has to be placed in a sealed reservoir to prevent it from
20 evaporation and the mixture surface has to be in vacuum or inert atmosphere to avoid its chemical reaction with air;
- the final volume of the polymer in the solid state is about 10 % smaller than the volume of the initial monomer in the liquid state;
- in order to obtain a polymer with good optical properties (low scattering and
25 high homogeneity), a constant external mechanical pressure has to be applied to the mixture during the entire prepolymerization reaction.

The cuvette (see Fig. 1) consists of two glass plates 1 and 2 separated by a tubular elastic ring 3 made from polyvinylchloride. Since methylmethacrylate is very aggressive chemically, the ring 3 is made from the material resistant to chemical action of
30 methylmethacrylate. Two glass plates 4 and 5 of parallelepiped shape are rigidly mounted between the plates 1 and 2 inside the ring 3. To prepare the sample with two

pairs of facets of a high optical quality, the surfaces of the plates 1 and 2 facing each other, and also the surfaces of the plates 4 and 5 facing each other, have to have high optical quality. When the cuvette is assembled, there is a sealed clearance inside the ring 3 and between the plates 1 and 2. Access to the clearance can be provided by means of two needles 6 and 7 that pierce the ring 3. The height h of the plates 4 and 5 is chosen to be slightly less than the gap H between the plates 1 and 2 determined by the elastic ring 3 in the unloaded state. This allows shift the plates 1 and 2 closer during prepolymerization process. This shift is necessary since during prepolymerization the volume of the mixture decreases by about 10 % compared with the initial volume and the mixture has to be under a constant mechanical pressure from the side of the plates 1 and 2.

Example of fabrication of the polymer of the present invention

Into 100 ml of a high-purity monomer of methylmethacrylate ($C_5H_8O_2$), the following components are added:

- 1 g of titanocendichlorid ($C_{10}H_{10}Cl_2Ti$) as a photoinitiator;
- 1 g of 2,2'-Azobis(2-methylpropionitril) ($C_8H_{12}N_4$) as a thermoinitiator;
- 10 g of nonlinear chromophore 3-methoxy-4,4'-nitrophenylazoanizole.

The obtained mixture is placed into the cuvette described above, which is preliminary filled with argon to prevent the contact between methylmethacrylate and oxygen of air. Argon is fed into the working volume of the cuvette through one of the needles, for example, the needle 6. The prepared mixture is fed into the cuvette through the other needle 7, argon being forced out through the needle 6. Thus the prepared mixture fills the cuvette without contacting the air. After the cuvette is filled with the prepared mixture, both needles 6 and 7 are pinched by, for example, pliers or special clamps to prevent extrusion of the prepared mixture from the cuvette.

Then the filled cuvette is placed into a special holder (see Fig.2) between plates 8 and 9 pulled together by springs 10. On the inner surfaces of the plates 8 and 9 have electrodes 11 and 12, respectively, connected to a voltage source 13. Alternatively, the electrodes 11 and 12 could be placed on the outer surfaces of the plates 1 and 2 and connected to the voltage source 13. The springs 10 provide compression of the plates 1 and 2 of the cuvette with a force of approximately $3-5 \text{ kg/cm}^2$.

The holder with the cuvette is placed into a heating chamber and kept there for 48 hours at the temperature of the order of 50°C. The thermoinitiator accelerating prepolymerization is initiated at this temperature.

During the first 4-5 hours the holder with the cuvette is rotated by 90° in different directions every 15-20 minutes. This is necessary to ensure a uniform distribution of the initial components of the mixture throughout the cuvette volume because the mixture at this stage is in the liquid state, and the mixture components may subside under their own weight.

After the indicated 4-5 hours of the prepolymerization reaction elapsed the methylmethacrylate monomer begins to turn into the polymethylmethacrylate polymer, and the reaction mixture starts to solidify. At this moment, the electric field with a strength of about 10^6 V/m is applied to the cuvette with the help of the voltage source and the electrodes 11 and 12. The constant action of the electric field results in alignment of long chromophore molecules along the direction of the applied field. The electric field is kept applied until the prepolymerization process is completed.

In 48 hours after its beginning the prepolymerization process is completed, and the sample finally solidified. As a result, approximately 90 % of the initial monomer of methylmethacrylate converts into the polymer of polymethylmethacrylate, and approximately 10 % of methylmethacrylate remains in the initial state, i.e., in the form of the monomer that is ready to react with the photoinitiator. The chromophore molecules become oriented in the direction of the applied external electric field and fixed in this position in the solidified matrix of the polymethylmethacrylate polymer. As a consequence, the prepared polymer sample became electrooptical, i.e., its refractive index varies with magnitude and direction of applied external electric field.

When the prepolymerization process is completed, the cuvette with the sample is naturally cooled to room temperature during 2-3 hours. The required cooling rate of not more than 0.25°C/min is provided by a large mass of the holder. After cooling, the sample is removed from the cuvette. The prepared polymer sample typically has the shape shown in Fig. 3. The surfaces 15 and 16 which contact with the plates 1 and 2, respectively, during prepolymerization, and also the surfaces 17 and 18 which contact with the plates 4 and 5, respectively, during prepolymerization have an optical quality.

The polymer sample 21 is finally shaped in the form of a parallelepiped by cutting unneeded parts along lines 19 and 20.

The entire fabrication process as well as storage of the sample has to be carried out in the dark.

5 A polymer material with several photoinitiators can be similarly fabricated. For example, accordingly to above procedure one can fabricate a material that has photosensitive properties in two spectral ranges (green region of the visible spectrum and UV). In order to do this the initial mixture shall include:

100 ml of a high-purity monomer of methylmethacrylate ($C_5H_8O_2$),
10 1 g of 2,2'-Azobis(2-methylpropionitril) ($C_8H_{12}N_4$) as a thermoinitiator;
10 g of nonlinear chromophore 3-methoxy-4,4'-nitrophenylazoanizole.
0,5 g of titanocendichlorid ($C_{10}H_{10}Cl_2Ti$) as a photoinitiator with sensitivity in green region of the visible spectrum;
0,5 g of 2,2-dimethoxy-2-phenylacetophenone - DMPA ($C_{16}H_{10}O_3$) as a
15 photoinitiator with sensitivity in UV region of the spectrum.

The photosensitive and electrooptical properties of the polymer sample prepared in accordance of the present invention were tested by recording a holographic diffraction grating in the sample and its subsequent readout through the Bragg diffraction of optical
20 radiation from this grating depending on external electrical field applied to the sample.

To record a diffraction grating (see Fig. 4), an interference pattern was formed in the sample 21 by two coherent light beams 22 and 23 directed onto the surface 15 at the angle θ . In the case the photoinitiator had the initial concentration indicated above, the sample 21 was illuminated with light during 5 s. The light intensity was 200 mW/cm^2
25 and the light wavelength $\lambda_w = 532 \text{ nm}$. The light initiated the photochemical reaction of the remaining 10 % of the methylmethacrylate monomer with the photoinitiator, during which a diffraction grating 24 was formed in the volume of the sample 21.

After being illuminated with the recording light, the sample 21 was kept in the dark for about 24 hours. After this period, the photochemical reaction was completed in
30 the previously illuminated portion of the sample and the photoinitiator and methylmethacrylate monomer molecules were removed from the nonilluminated sites in

a natural way – by diffusing into the environment. During the reaction, local variations of the material density arose in the illuminated portion of the sample, which, in turn, resulted in local variations of the refractive index, i.e., recording of the diffraction grating 24 in the sample 21 was performed. The period Λ of the grating 24 is given by a well-known expression:

$$\Lambda = \frac{\lambda_w}{2 \sin \theta}. \quad (1)$$

In this example of recording a diffraction grating the indicated above initial components proportion of fabricated polymer and exposure parameters allow obtaining the grating diffraction efficiency of the order of 90 %.

10 If the prepared sample is not used immediately for light exposition, for example, grating recording, it should be kept at a temperature not higher than -25°C.

Note that the sample loses photosensitive properties after a hologram is recorded and the photochemical reaction is completed because all the photoinitiator has reacted with methylmethacrylate in the illuminated portion of the sample and diffused out of the nonilluminated portion. This means that the photosensitive properties of the obtained polymer can be used only once.

The holographic sensitivity of the prepared polymer sample is defined as the energy needed to record a holographic diffraction grating with a diffraction efficiency of 1 %. The holographic photosensitivity of the fabricated material was determined by a conventional procedure. The procedure is as follows. Holograms are recorded at in the material under test with different recording energies (the recording energy is the product of the recording light intensity, in W/cm², and recording time, in seconds). Typically the recording time is set constant, while the light intensity is varied. Then the dependence of the grating diffraction efficiency on the recording energy is measured. The recording energy that provides 1 % diffraction efficiency is taken as the holographic sensitivity. In our case, to form a grating with a diffraction efficiency of 1 %, the recording energy of about 20 mJ/cm² was needed. Note that it is comparable with the holographic sensitivity of a heavily doped lithium niobate sample. The above measurements were done for the diffraction grating with a length of 1 cm.

To estimate the electrooptical properties, let us consider a diffraction grating recorded in an electrooptical material. When it is illuminated with a light beam in the direction parallel to the diffraction grating vector, the light with the wavelength satisfying the Bragg condition is backreflected from the grating. Strictly speaking, the grating reflects the light in a specified narrow wavelength range $\Delta\lambda_r$ with its central wavelength λ_r satisfying the Bragg condition:

$$\lambda_r = 2n\Lambda, \quad (2)$$

where n is the average refractive index of the electrooptic material; and Λ is the diffraction grating period.

It is known that the average refractive index n in the electrooptic material depends on the strength E of the applied electric field:

$$\Delta n = \frac{n^3 r_{eff} E}{2}, \quad (3)$$

where Δn is the refractive index variation;

n is the average refractive index at $E = 0$; and

r_{eff} is the effective electrooptic coefficient.

Thus it is evident that by varying the electric field applied to the sample, one can vary the refractive index of the material. As a result, the Bragg condition will not be satisfied for λ_r , and therefore the detected power of the light beam at λ_r reflected from the grating will decrease. As the applied field increases the detected signal becomes zero.

Taking into account the fact that, for the grating with a rectangular envelope of the refractive index modulation the dependence of the diffraction efficiency on the applied

electric field is proportional to the function $\frac{\sin(x)}{x}$, where x is the parameter

proportional to the strength of the applied electric field. Under this condition of attaining the zero detected signal, the variation in the refractive index Δn_B caused by the applied

electric field can be defined as:

$$\Delta n_B = \frac{\lambda_r}{2T}, \quad (4)$$

where T is the grating length.

Thus by measuring the electric field E applied to the sample that corresponds to the zero optical power reflected from the grating and knowing the sample length, one can find the effective electrooptic coefficient r_{eff} through Eqs. (3) and (4).

5 In the experiments (see Fig. 5), hologram readout was done in reflection geometry. The polymer sample 21 with the recorded diffraction grating 24 was illuminated from the sample side 17 with a laser beam 25, and the light beam 26 reflected from the grating 24 was detected. Readout was performed at the wavelength of the order of 1500 nm, and the period of the grating 24 satisfied the Bragg condition in the absence of the external
10 electric field. The external field was applied to the sample with the help of electrodes 27 and 28. When the electric field was applied, the average refractive index of the sample changed and, hence, the Bragg condition was violated and the readout beam intensity changed. By measuring the dependence of the power of the light beam 26 reflected from the grating 24 on the electric field strength according to the procedure indicated above,
15 the effective electrooptic coefficient r_{eff} was determined. It was found to be equal to $(2 \div 3) \cdot 10^{-12}$ m/V.

Thus the present invention provides fabrication of electrooptical photosensitive polymers based on polymethylmethacrylate in wide range of electrooptical and photosensitive parameters suitable for use as an optical material.

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CLAIMS

1. An electrooptical photosensitive polymer material, comprising:

an electrooptical chromophore, from 10 to 30 percent;

a photoinitiator, from 1 to 5 percent; and

5 a product of methylmethacrylate prepolymerization, from 65 to 89 percent, wherein said prepolymerization product contains polymethylmethacrylate and an unreacted methacrylate monomer.

3. The composition of claim 1 wherein said electrooptical chromophore is selected
10 from the group consisting of 2,5-dimethyl-4,4'-nitrophenylazoanisole, 3-methoxy-4,4'-nitrophenylazoanisole and ring-locked phenyltertaene bridged chromophore.

4. The composition of claim 1 wherein said photoinitiator is selected from the group consisting of titanocene dichloride and 2,2-dimethoxy-2-phenylacetophenone
15

5. The composition of claim 1 wherein said electrooptical chromophore molecules have the same polar orientation.

6. The composition of claim 1 wherein said polymer material contains multiple
20 photoinitiators with all the photoinitiators having their spectral selectivity at different spectral ranges.

7. The composition of claim 1 wherein said photoinitiator and said electrooptical chromophore are selected depending on the wavelength range in which the proposed
25 polymer material will be used.

8. A method for producing an electrooptical photosensitive polymer material comprising the steps of:

adding a photoinitiator and an electrooptical chromophore to a high-purity
30 monomer of methylmethacrylate forming a mixture;
stirring said mixture thereby producing a homogeneous mixture;

placing said homogeneous mixture within a cuvette providing for prepolymerization of said homogeneous mixture, wherein said cuvette prevents access of air to said homogeneous mixture during said prepolymerization and heats said homogeneous mixture at a constant elevated temperature of about 50° C during said prepolymerization;

applying an electrical field until such time as said prepolymerization is complete; cooling said prepolymerized mixture.

9. The method of claim 8 further comprising the step of adding a thermoinitiator to said mixture, wherein said thermoinitiator accelerates said prepolymerization.

10. The method of claim 9 wherein said thermoinitiator is 2,2'-Azobis(2-methylpropionite).

11. The method of claim 10 wherein said thermoinitiator is added in a concentration of up to 1%.

12. The method of claim 8 wherein said electrooptical chromophore is selected from the group consisting of 2,5-dimethyl-4,4'-nitrophenylazoanisole, 3-methoxy-4,4'-nitrophenylazoanisole and ring-locked phenyltertaene bridged chromophore.

13. The method of claim 8 wherein said photoinitiator is selected from the group consisting of titanocene dichloride, 2,2-dimethoxy-2-phenylacetophenone

14. The method of claim 8 wherein said mixture is kept under a constant external pressure of approximately 3-5 kg/cm² during said prepolymerization.

15. The method of claim 8 wherein said method for producing an electrooptical photosensitive polymer material is carried out in the dark.

16. An apparatus for fabricating an electrooptical photosensitive polymer comprising:

a first glass plate and a second glass plate, said glass plates having an outer surface and an inner surface and said inner surfaces being separated by a tubular elastic
5 ring;

a third glass plate and a fourth glass plate mounted upon said inner surface of said first and second glass plate, wherein said third and four glass plates are of parallelepiped shape and are rigidly mounted opposite each other between said first and second glass plates and inside said tubular elastic ring;

10 a first needle and a second needle wherein said needles pierce said tubular elastic ring allowing for the introduction of gases and liquid mixture;

a first holder plate and a second holder plate having an inner surface and an outer surface, wherein a first electrode and a second electrode are mounted upon said inner surface of said first and second holder plates; and

15 a first spring and a second spring said springs being mounting upon said inner surface of said holder plates and allowing for compressive forces between said plates.

17. The apparatus of claim 16 wherein said springs provide a compressive force of approximately $3\text{-}5\text{ kg/cm}^2$.

20

18. The apparatus of claim 16 wherein said tubular elastic rings is made of polyvinylchloride.

19. The apparatus of claim 16 wherein said glass plates have high optical quality.

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20. The apparatus of claim 16 wherein said electrodes are connected to a voltage source.

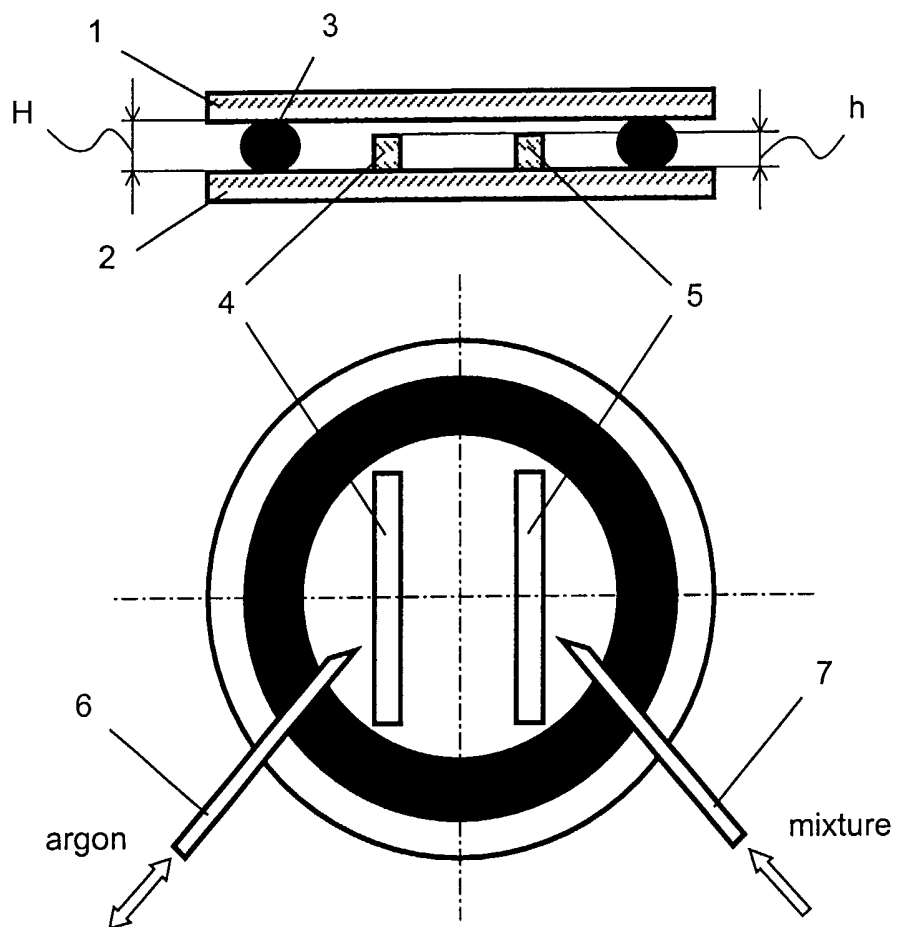


Fig. 1

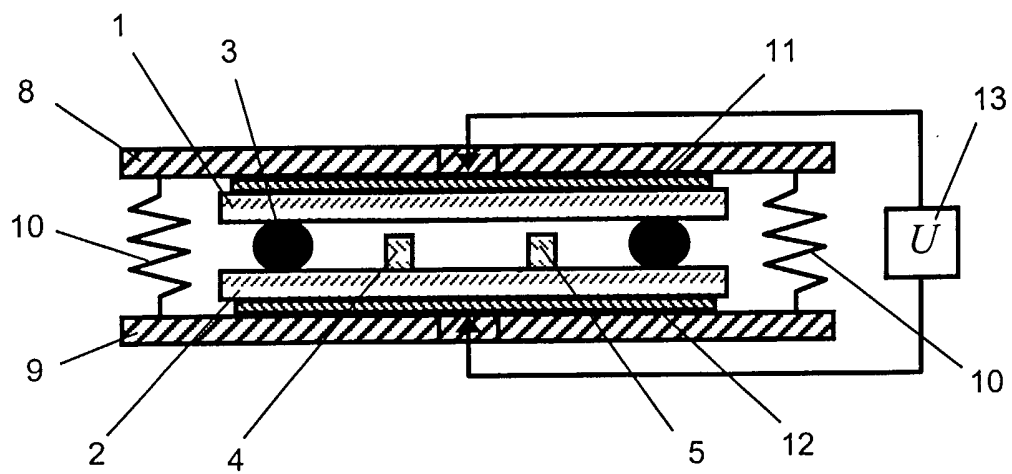


Fig. 2

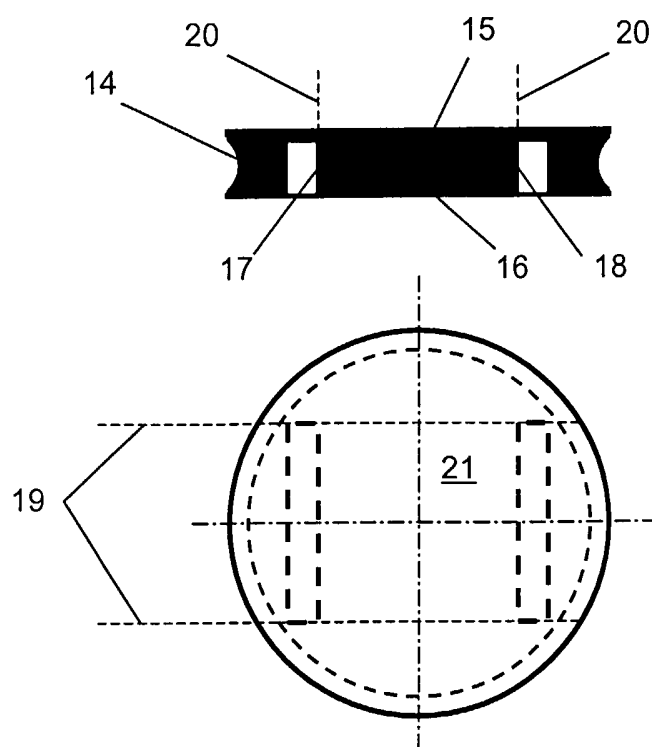


Fig. 3

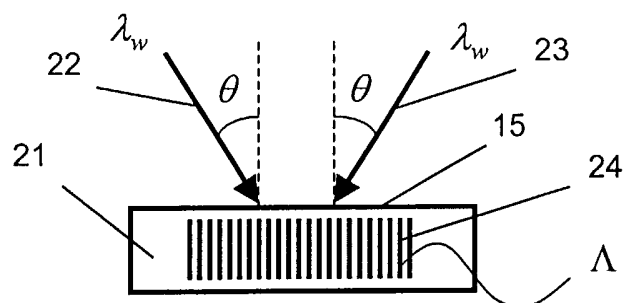


Fig. 4

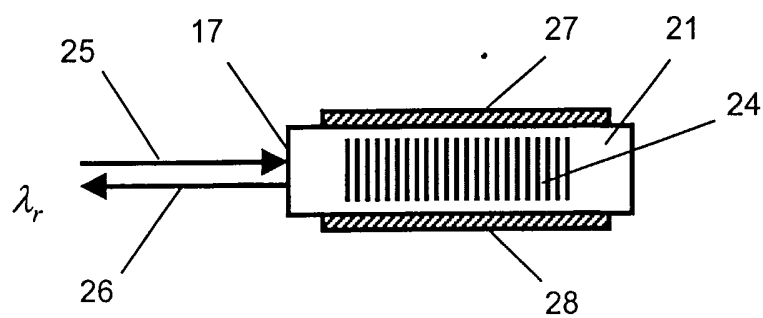


Fig. 5