

Low temperature anomalies in polyvinyl alcohol photopolymers

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Acoustooptical parameters in a mixture of polyvinyl alcohol (PVA) polymers with modified polyvinyl alcohol (MPA) were investigated as functions of the MPA content, time of exposure and temperature. The maximum value of the acoustooptical quality coefficient was achieved for values of the MPA content above 70%. It was proposed to use the polyvinyl alcohol photopolymers as acoustooptical modulators and deflectors. An essential influence of the polyvinyl alcohol modifications on the acoustooptical parameters was unambiguously shown. Also, a critical dependence of the acoustooptical coefficients on the sample thickness was revealed. The data on the acoustooptical quality coefficient correlate well with the data obtained for the sound losses coefficient. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The modified polyvinyl alcohol photopolymers are one of the most important classes of synthetic linear polymers¹. Their essential advantages include high mechanical properties and a possibility to modify their features in a required direction by synthesis in combined polyamide systems. Water-swollen and water-soluble photopolymers, produced in this manner, can find wide applications^{2,3} in practice. The acoustooptical investigations of such materials may also lead to the creation of new classes of quantum electronics materials.

However, there have been few investigations to date devoted to the possible use of the modified polyvinyl alcohol photopolymers in different acoustooptical devices. On the other hand, these materials usually show good optical as well as elastic properties. Therefore, we have predicted and proposed their possible applications as materials for acoustooptical deflectors and modulators.

A new phenomenon was recently discovered which consists in occurrence of the optical second harmonic generation in these complex PVA photopolymers under

the influence of laser light⁴. The main purpose of this article consists in investigations of an acoustooptical quality parameter M and a corresponding sound losses parameter K in the mentioned photopolymers. This is necessary to study their usefulness as the light modulators and deflectors which play an essential role in creation of new acoustooptical devices.

The most important features of the modified polyvinyl alcohol photopolymers consist of a wide spectral range of optical transparency and a weak sensitivity to higher temperatures. Therefore, devices made from these materials can be used in a wide range of environmental conditions. Moreover, it is possible to improve further the modified optical properties of polyvinyl alcohol photopolymer by the applications of an external electric field.

EXPERIMENTAL

An apparatus for these investigations was set up based on a polarized laser from which light propagates through a half-wave plate and polarizer and then falls on the test specimen mounted on a rotating table (see *Figure 1*). The latter is fitted with a nonius scale and the sample is inserted into a thermoregulated cryostat which allows us

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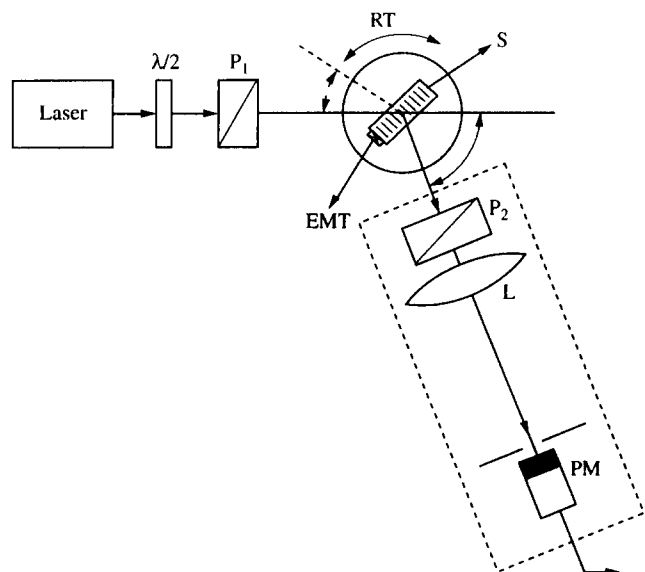


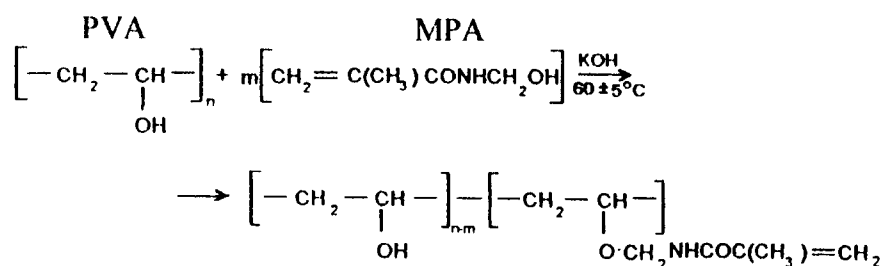
Figure 1 Experimental set up for investigations of the acoustooptical quality coefficient *M*

to change the temperature between 4.2 K and 500 K. The travelling acoustical wave is excited by an electro-mechanical LiNbO₃ transducer. Intensity of the diffracted light is measured using an optical system consisting of an analyser, a gathering lens and a photomultiplier. The signal is detected using a micro-computer operating in the CAMAC PDP system. The light diffraction is observed for the volume elastic waves as well as the surface elastic waves. It was shown that the diffraction can be observed both in the transparent and reflected light geometry if the light incident angle lies between 20° and 22°.

The synthesis of a mixture of the PVA and the MPA was performed in three steps. At first, a methylol-methacrylamide was formed by the reaction between methacrylic acid and its *trans*-paraform. The synthesis was performed in a three-necked reactor filled with the mechanical mixtures at temperatures of 40 ± 5°C for 45 min in the presence of KOH catalyst.

The following component content was used: 49 g (0.5 mol), amide of the methacrylate oxide; 17 g (0.5 mol), amide of the methacrylate oxide; 2.5 g (0.1 mol), paraform. The amount of the catalyst should not exceed 0.5% of the methacrylate acid amide. The reaction product was filtered and dried in air between 20°C and 30°C for 12 h. The PVA-MPA mixture was synthesized in the next step using a solution of the MPA and water at a temperature of 60°C within 5 h. Solutions with different ratios of the PVA/MPA were obtained.

The synthesis of the aforementioned photopolymers was performed by the chemical reaction scheme:



where *m* and *n* are the integer numbers. More detailed information concerning the technological procedure is presented in refs 5 and 6.

The ultrasound waves cause periodic changes of density in the PVA-MPA photopolymers that results in a periodic change of the refractive index analogous to a diffraction grating with the same period as the ultrasound wave and which propagates with the sound velocity. The diffraction beam and its intensity is dependent on the acoustical parameters (amplitude and frequency). We have shown that the best transformation features were obtained for sound frequencies of about 50 MHz.

The solid photopolymers were obtained by a through illumination of the above mentioned photocompositions using a u.v.-hydrogen lamp with a light power density of about 45 W cm⁻² and applying different u.v.-light exposure times. Our previous investigations have shown that the optimum exposure time lies between 5 min and 7 min for the PVA-MPA samples.

THEORETICAL DETAILS

The materials chosen for acoustooptical modulators and deflectors should, first of all, ensure the necessary efficiency of the interaction between light and sound. This efficiency is determined by a ratio of the transparent to the incident light intensities and it can be calculated using the expression

$$\eta = \frac{\pi n^6 p^2}{2 \rho \theta^3} \frac{P_a d}{H \lambda^2 \cos^2 \Theta} \quad (1)$$

where *p* is the photoelastic constant, λ is the light wavelength in vacuum, *P_a* is the acoustical beam power, *d* is the distance of light propagation through the acoustical beam. A change of the electrical susceptibility as a function of the deformation *S* can be expressed as

$$\Delta B = pS \quad (2)$$

A change of the refractive index for the photopolymers takes the form

$$\Delta n = -\frac{n^3}{2} pS \quad (3)$$

It is well known that the deformation *S* is connected with the power of the acoustical wave by the relation

$$W_a = \frac{1}{2} \rho \theta^3 S S^* dH \quad (4)$$

where *S** is a complex conjugation of *S*. We have finally that

$$\Delta n = -n^3 p \left(\frac{W_a}{2 \rho \theta^3 dH} \right)^{1/2} \quad (5)$$

After simple substitutions, we have obtained

$$I_1 = \sin^2 \left[\frac{\pi}{\lambda \cos \Theta} \left(\frac{MW_a d}{2H} \right)^{1/2} \right] \quad (6)$$

with $M = n^6 p^2 / \rho \theta^3$, where M is known as the so-called coefficient of the acoustooptical quality and its value determines the intensity of the diffraction light independently of any interaction geometry.

Besides possessing the greatest efficiency of the light-sound interaction, acoustooptical crystals should also work well in a wide frequency region of the acoustical waves for a constant incident angle θ . This can be provided for by using the light and acoustical beams of a defined scattering length. On the grounds of the theoretical estimations, a more convenient situation appears when the above-mentioned angles are equal. In the latter case the efficiency of the interaction η , the main frequency f_0 and the band dispersion Δf are connected by the expression

$$\eta f_0 \Delta f = \left(\frac{n^7 p^6}{\rho \theta} \right) \frac{\pi^2 W_a}{\lambda_0^3 \cos \Theta} \quad (7)$$

where Δf defines a region of the frequencies in which the intensity decrease of the refracted light is equal to about 3 dB. The diffraction phenomena disappear with increasing frequency of the acoustical wave and increasing angles of the incident light. The light beams of the zero-th and the first orders begin to play a main role.

It is necessary to note that we deal with essentially nonuniform samples in the case of the photopolymers due to peculiarities of their photopolymerization. Therefore, we should take into account a space distribution of the corresponding optical constants depending on the position vector \mathbf{r} . In traditional plane wave approximation, the refractive index n can be presented in the form

$$n(\mathbf{r}, t) = n + \Delta n \exp i(\omega t - \mathbf{k}\mathbf{r}) \quad (8)$$

where $n(\mathbf{r}, t)$ describes the time and spatial dependence of the refractive index and Δn is the acoustooptical induced amplitude of the corresponding refractive index. The induced electric field is periodic in time and space with the periods determined by the acoustical wave and the photopolymer parameters. The electric field intensity can be expanded in a Fourier series

$$\mathbf{E} = \sum_{n=-\infty}^{\infty} E_m(\mathbf{r}) \exp [i[(\Omega + m\omega)t - \mathbf{K}_m \mathbf{r}]] \quad (9)$$

where $\mathbf{K}_m \mathbf{r} = (2\pi/\Lambda)\mathbf{r}\mathbf{e}$, \mathbf{K}_m and Ω are wavevector and angular frequency of the light wave, respectively, and $E_m(\mathbf{r})$ is an amplitude of the diffracted light of the m th order with the frequency of $(\Omega + m\omega)$. After substitution of equations (2) and (3) into equation (1), one can receive the following set of equations

$$\frac{dE_m}{d\phi} + \frac{\xi}{2L} (E_{m+1} - E_{m-1}) = -i \frac{mk}{\cos \phi} (\sin \phi_0 - m \sin \phi_0) E_m \quad (10)$$

where \mathbf{k} is a wavevector of the optical wave in vacuum. A solution of this equation can be written in the form

$$\mathbf{E}(\mathbf{r}) = \exp(-\frac{1}{2}im \mathbf{k}\mathbf{r} \operatorname{tg} \phi_0) J_m \left[\xi \frac{\sin(\mathbf{k}\mathbf{r} \operatorname{tg}(\phi_0/2))}{\mathbf{k}\mathbf{e} \operatorname{tg}(\phi_0/2)} \right] \quad (11)$$

where $J_m(x)$ is Bessel function of the m th order.

The normalized intensity of the diffracted beam of the m th order depending on a distance l is determined within the photopolymer volume by the expression

$$I_m = E_n(l) E_m^*(l) = J_m^2 \left(\xi \frac{\sin |\mathbf{r}|}{|\mathbf{r}|} \right) \quad (12)$$

where $|\mathbf{r}| = \mathbf{k}l \operatorname{tg}(\phi_0/2)$. The diffraction phenomena disappear with increasing frequency of the acoustical wave and for the angles of incident light $\phi_0 \cong \phi_B$ when the main role has begun to be played by the light beams of the zero-th and of the first orders. In the latter case, the corresponding equations are simplified (at $\phi_0 \rightarrow \phi_B$) to the form:

$$\begin{aligned} \frac{dE_0}{dr} &= -\frac{\xi}{2l} E_1 & (13) \\ \frac{dE_1}{dr} + i \frac{2\xi}{r} E_1 &= \frac{\xi}{2l} E_0 \end{aligned}$$

where

$$\xi = \frac{\mathbf{k}l(\sin \phi_0 - \sin \phi_B)}{2 \cos \phi_0}$$

These equations can be solved as shown below

$$\begin{aligned} E_0(\mathbf{r}) &= \exp\left(\frac{-i\xi\mathbf{r}}{l}\right) \\ &\times \left[\cos\left(\frac{\mathbf{r}}{l} \sqrt{\xi^2 + (l/2)^2}\right) + i \frac{\xi}{\sqrt{\xi^2 + (l/2)^2}} \right. \\ &\times \left. \sin\left(\frac{\mathbf{r}}{l} \sqrt{\xi^2 + (l/2)^2}\right) \right] \quad (14) \end{aligned}$$

The normalized intensities (for $\mathbf{r} = l$) are equal to:

$$J_1 = 1 - J_0 = \left(\frac{\xi}{2\chi}\right)^2 \sin^2 \chi \quad (15)$$

where $\chi^2 = \xi^2 + (\xi/2)^2$.

The photopolymer acoustooptical materials can ensure a good efficiency of the interaction between light and sound as mentioned above. During phase transitions there arise changes in the electron as well as the quasi-phonon subsystems that leads to a corresponding modification of the total acoustooptical parameter M .

RESULTS AND DISCUSSION

We have performed the acoustooptical investigations of the PVA-MPA photopolymers at different temperatures, particularly at low temperatures, where we have previously shown phase transitions⁵. Dependence of the acoustooptical quality coefficient of M on the sample thickness d is presented in Figure 2 for the samples with different content of the MPA. It is clearly seen that a maximum value of the M coefficient is reached for the sample thickness of about $5 \mu\text{m}$ to $7 \mu\text{m}$. This reflects an essential role of the surface states in the thin samples (or thin films) where the nature of the chemical bounds can play an essential role in determination of the acoustooptical coefficient.

Another important technological parameter is the sound losses coefficient K which is presented in Figure 3 as a function of the sample thickness. It is clearly seen that the sound losses coefficient reaches a minimum value at the same position as the quality coefficient M

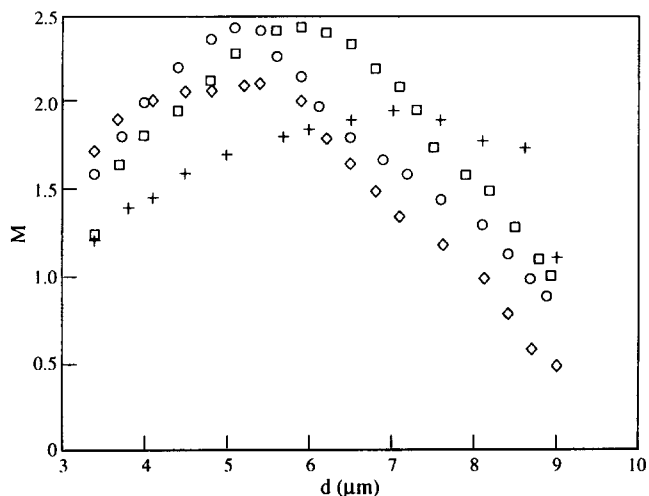


Figure 2 Dependence of the acoustooptical quality coefficient M (in arbitrary units) on sample thickness d (in μm) for the photopolymers with different content of the MPA: \circ , 20%; \square , 40%; \diamond , 60%; +, 80%

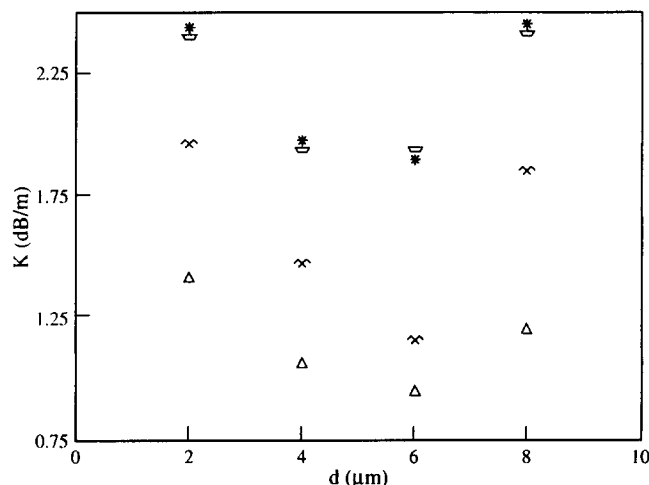


Figure 3 Dependence of the acoustical losses coefficient K (in dB m^{-1}) on sample thickness d (in μm) for the samples with different PVA-MPA compositions: \triangle , 20%; \times , 40%; $*$, 60%; $=$, 80%

maximum. Moreover, the acoustooptical quality coefficient M increases with electric field intensity increasing from 10 kV cm^{-1} to $10\,000 \text{ kV cm}^{-1}$ as depicted in *Figure 4*.

Such behaviour reflects, in our opinion, an increasing structural ordering of the aromatic rings in the applied electric field. These data are in good agreement with those obtained by us previously using nonlinear optical methods⁴. It is clearly seen that the corresponding maximum of the acoustooptical quality coefficient M is shifted towards higher thicknesses with increasing MPA concentration that compares with results on the polyurethanes⁷.

Following the pattern of behaviour of the acoustooptical quality, the dependence of the acoustical losses is

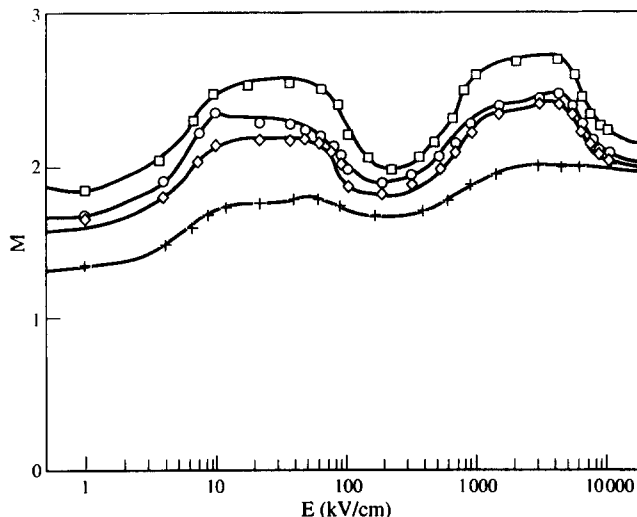


Figure 4 Dependence of the acoustooptical quality coefficient M (in arbitrary units) on external electric field intensity E (in kV cm^{-1}) for the sample thickness of $5 \mu\text{m}$ and for different PVA-MPA compositions: \circ , 20%; \square , 40%; \diamond , 60%; +, 80%

also smallest for the MPA concentration of about 60%. Therefore, we recommend the above optimum composition of the PVA-MPA system (i.e. about 60% of the MPA) for preparation purposes of acoustooptical modulators as well as deflectors.

CONCLUSIONS

The investigations performed by us have unambiguously shown the possibility of using specific PVA-MPA photopolymer mixtures as photoacoustical modulators and deflectors. The proposed photopolymers can be used as materials operating for light spectra in the visible spectral region in contrast to the traditional crystalline samples. The optimum thickness of the specimen should lie between $5 \mu\text{m}$ and $7 \mu\text{m}$. We have also shown that electric field intensity substantially influences the acoustooptical coefficients.

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