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13. ABSTRACT (Maximum 200 words)

Poly{4,4'-(1-methylethylidene)bisphenylene 3-[4-(4-nitrophenylazo)phenyl]-3-aza-pentanedioate} (pMNAP) was synthesized through the condensation polymerization of 4,4'-isopropylidene-bis-phenol and N-[4-(4-nitrophenylazo)phenyl]imido diacetyl chloride. The polymer solution in tetrahydrofuran (THF) was spin-coated onto a glass substrate to form a film and the process of reversibly photoinduced birefringence was tested. The birefringence induced in the film was observed at a level of 0.04. The biexponential fitting of the birefringence growth and relaxation curves shows two kinds of processes. A fairly low birefringence relaxation occurs after the light is turned off, about 12% at room temperature and less than 50% at 138°C, close to the glass transition temperature (152°C). pMNAP decomposes at about 160°C which prevents its use as a material for optical storage. ©1996 John Wiley & Sons, Inc.

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Azo Polymers for Reversible Optical Storage. 11. Poly{4,4'-(1-Methylidene)Bisphenylene-3-[4-(4-Nitrophenylazo)Phenyl]-3-Aza-Pentanedionate}

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Azo Polymers for Reversible Optical Storage. II Poly{4,4'-(1-Methylethylidene)Bisphenylene 3-[4-(4-Nitrophenylazo)Phenyl]-3-Aza-Pentanedioate}

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SYNOPSIS

Poly{4,4'-(1-methylethylidene)bisphenylene 3-[4-(4-nitrophenylazo)phenyl]-3-aza-pentanedioate} (pMNAP) was synthesized through the condensation polymerization of 4,4'-isopropylidene-*bis*-phenol and *N*-[4-(4-nitrophenylazo)phenyl]imido diacetyl chloride. The polymer solution in tetrahydrofuran (THF) was spin-coated onto a glass substrate to form a film and the process of reversibly photoinduced birefringence was tested. The birefringence induced in the film was observed to a level of 0.04. The biexponential fitting of the birefringence growth and relaxation curves shows two kinds of processes. A fairly low birefringence relaxation occurs after the light is turned off, about 12% at room temperature and less than 50% at 138°C, close to the glass transition temperature (152°C). pMNAP decomposes at about 160°C which prevents its use as a material for optical storage. © 1996 John Wiley & Sons, Inc.

Keywords: azo polymers • optical storage • photoinduced birefringence • polyester • birefringence growth and relaxation kinetics

INTRODUCTION

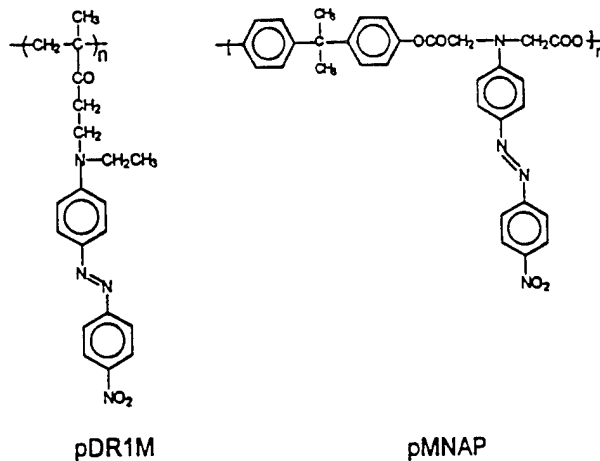
Polymers containing substituted azobenzene groups are being studied as optical storage materials. Anisotropy can be induced by the orientation of azobenzene groups when exposing a polymer film to a linearly polarized laser and can be eliminated by a circularly polarized laser. The mechanism of 'writing' and 'erasing' involves photochemically excited trans-cis isomerizations and photochemical and/or thermal cis-trans isomerizations of the azobenzene groups. When shining a linearly polarized laser on a polymer film, the azo groups which are not perpendicular to the laser polarization direction will undergo many trans-cis-trans isomerization cycles accompanied by reorientations until they fall in one of the directions (in a plane) perpendicular to the laser polarization direction at the end of one of the cis-trans isomerizations. The net result is an ori-

entation distribution with an excess of azo groups in the direction perpendicular to the laser polarization. This orientation can be detected as birefringence by another laser beam. When an oriented spot in a polymer film is irradiated by a circularly polarized laser or heated above the glass transition temperature (T_g) of the polymer, the anisotropy will be 'erased' back to the random state of the 'unwritten' area.¹⁻³ This is because the azo groups in all directions except those parallel to the laser beam direction are activated by the laser. This kind of laser-induced and eliminated orientation may take place in liquid crystalline and amorphous polymers as well as in semicrystalline polymers.¹⁻¹⁴

The optical response of the polymer is strongly influenced by its structure since the writing and erasing are based on the azo chromophore motions. In our previous studies,^{1,7,9} we found that the rate of achieving birefringence and the level of induced birefringence depend on the type and the size of the azo groups. The bulkier azo side chain with a nitronaphthalene unit moves slower than the azo with a nitrobenzene unit due to the steric effect.⁷ The

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alignment of azo groups is also affected by the segmental and main chain motions.⁷ A high T_g polymer may show a more stable orientation, since the motions of the side chains and of the main chain are related to the difference between the operating temperature and T_g . It is preferable to investigate polymers with higher T_g for the reversible optical storage process. We report the synthesis of a polyester, poly{4,4'-(1-methylethylidene)bisphenylene 3-[4-(4-nitrophenylazo)phenyl] - 3 - aza - pentanedioate} (pMNAP) and its photoinduced birefringence. Comparison is made with poly{4'-[(2-(methacryloyloxy)ethyl)ethylamino] - 4 - nitroazobenzene} (pDR1M). The structures of the two polymers are shown in Scheme 1.



Scheme 1.

9 pt space

EXPERIMENTAL

4,4'-Isopropylidene diphenol (bisphenol A) was purchased from Aldrich and was dried in the vacuum oven overnight at 60°C before use. 1,2-Dichloroethane (BDH) was distilled and stored under 3A molecular sieves. Aniline diacetic acid was prepared according to the literature procedure.¹⁵

3-[4-(4-Nitrophenylazo)phenyl]-3-aza-pentanedioic acid (II) was synthesized by a method similar to the one reported in the literature¹⁶ and recrystallized from methanol, mp. 171°C (dec.). ¹H nuclear magnetic resonance (NMR) (dimethylsulfoxide [DMSO-*d*₆], δ in ppm): 4.28 (s, 4H, —CH₂—), 6.78 (*d*, 2H, aromatic, ortho to the amine group), 7.85 (*d*, 2H, aromatic, meta to NO₂), 7.95 (*d*, 2H, aromatic, meta to amine group), 8.37 (*d*, 2H, aromatic, ortho to NO₂).

Poly{4,4'-(1-methylethylidene)bisphenylene 3-[4-(4-nitrophenylazo)phenyl] - 3 - aza - pentanedioate} (pMNAP): A mixture of 1.8225 g (4.733 mmol) Compound II, 10 mL benzene and 25 mL thionyl chloride in a 100 mL round-bottom flask was heated to boiling for about 20 min until a clear solution formed and then the solvent and most of thionyl chloride were distilled off. The residue of thionyl chloride was then pumped out. To the black red solid obtained, 10 mL 1,2-dichloroethane was added and then heated to get a clear solution. A mixture of 1.1621 g (4.733 mmol) bisphenol A and 1.55 mL triethyl amine in 25 mL 1,2-dichloroethane was added to the above solution while stirring. After stirring at 60°C for 15 h, the reaction mixture was cooled and filtered (to separate the salt and some insoluble product). The filtrate was poured into methanol and the precipitate was collected and reprecipitated from a THF/methanol system. The

polymer was then dried in a vacuum oven overnight (yield 73%), molecular weight 5.6×10^3 [gel permeation chromatography (GPC), relative to monodisperse polystyrene]. A ¹H-NMR spectrum (DMSO-*d*₆) is shown in Figure 1. The peak labeled *c** is assigned to the aromatic proton next to —OH in the bisphenol A end group of the polyester, confirming the low molecular weight of the product.

The films were prepared by spin-coating from THF solution onto a glass substrate and dried in vacuum for 20 h at 100°C. The film thickness was 400–500 nm measured by interferometry. The procedure for reversibly inducing birefringence with a laser beam on the polymer film was described previously.² Writing and erasing were performed using an argon laser (488 nm) intensity of 6 mW on a spot of 2 mm in diameter at room temperature or at variable temperatures adjusted by a heating stage. Thermal transitions were measured on a Mettler TA-30 DSC instrument equipped with a TA-3000 processor at the scan rate of 20°C/min. The electronic spectra were recorded on a Shimadzu Spectrometer. The molecular weights of the polymers were estimated by gel permeation chromatography. A Waters Associates liquid chromatography was equipped with a Model R401 differential refractometer and Model 440 absorbance detector. THF was used as the eluent. The ¹H-NMR spectra were obtained on a Bruker AC-F 200 NMR spectrometer.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Polymer

Scheme 2 gives the synthesis route for polyester pMNAP. The azo-containing diacid chloride is syn-

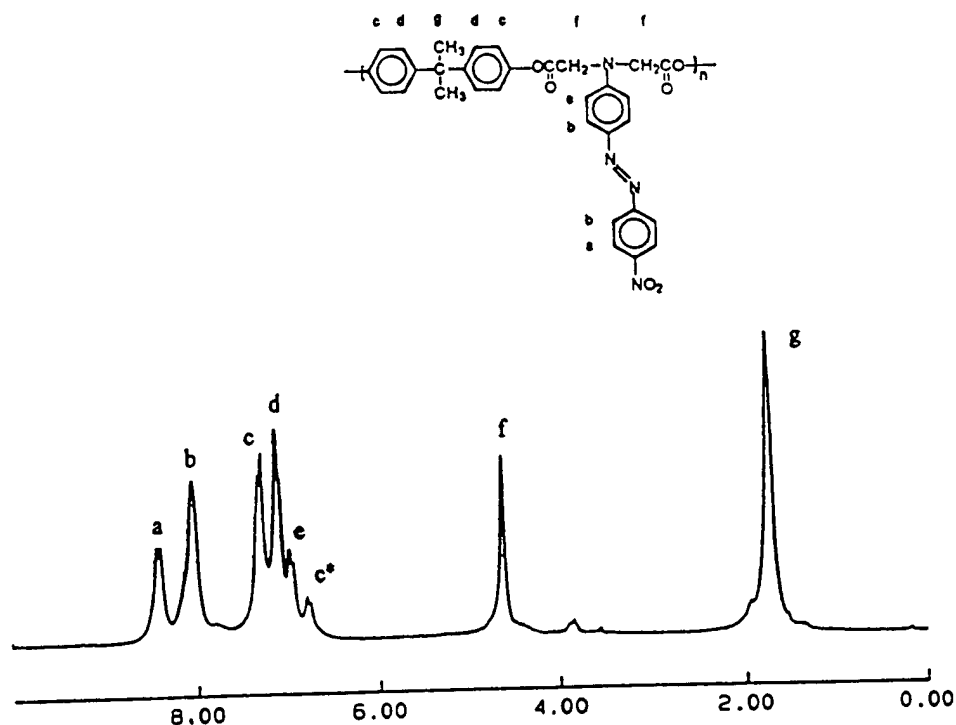
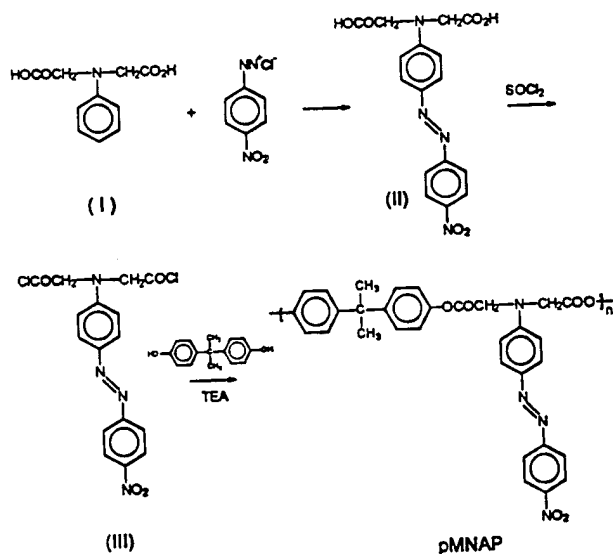


Figure 1. ^1H NMR spectrum of pMNAP in $\text{DMSO}-d_6$ at room temperature. The assignments are given on the spectrum, peak c^* is assigned to the aromatic proton next to $-\text{OH}$ in the bisphenol A end group of the polyester.

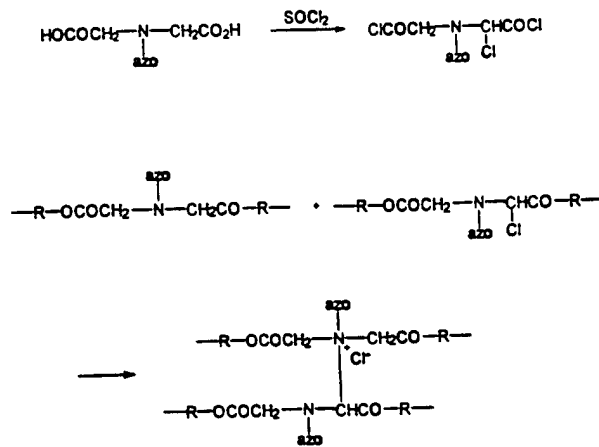
thesized according to the literature¹⁶ and the condensation polymerization is carried out without isolation of the diacid chloride monomer. The polymer is obtained as a yellow brown solid, yield 73%. Some byproduct is found during the polymerization which is insoluble in water, methanol, dioxane, and even



Scheme 2.

THF. It is probably the crosslinking product from the reaction of the amine group with the α -chloro-substituted diacid chloride that formed when converting the diacid to diacid chloride (II to III), as shown in Scheme 3. FTIR spectra of the insoluble polymer shows a band at 542 cm^{-1} which is probably the chlorine-carbon stretch.¹⁷ The structure of the insoluble byproduct has not been determined.

pMNAP has a maximum electronic absorbance at 450 nm in DMSO solution and at about 425 nm



Scheme 3.

in film as shown in Figure 2. These wavelengths are lower than those of pDR1M, which are about 476 nm in solution and 458 nm in film, respectively.^{7,18} The difference is due to the lesser electron-donating character of the amino group in pMNAP in comparison to the amino group in pDR1M, since $-\text{CH}_2\text{COOR}$ has less electron-giving ability than $-\text{CH}_2\text{CH}_2\text{OR}$ and $-\text{CH}_2\text{CH}_3$. Therefore the intramolecular charge transfer in the azobenzene groups of pMNAP is weaker than that in pDR1M and the maximum electronic absorbance shifts to a shorter wavelength.

pMNAP films are amorphous, as proven by polarized microscopy. The DSC curve of the polymer shows a glass transition temperature at 152°C followed immediately by exothermic decomposition.

Photoinduced Birefringence

A typical writing-relaxation-erasing curve is obtained when subjecting the film to illumination with a 488 nm writing-erasing laser beam and using a 633 nm reading laser beam at room temperature (Fig. 3). The linearly polarized laser beam is turned on at point A and the birefringence is rapidly induced and reaches a saturated level. The birefringence relaxes at point B, where the writing beam is turned off, and reaches a stable level around point C. The induced birefringence is then completely eliminated with turning on a circularly polarized light at point C, and the film is ready to be rewritten in the same manner. The saturated value of the photoinduced birefringence is about 0.038, which is much lower than the maximum birefringence achieved in pDR1M (0.1)⁷ or poly{4'-[(2-(acryloyloxy)ethyl)ethylamino]-4-nitroazobenzene} (pDR1A) (~0.08).³ Several factors may be responsible for this difference. The first may be the difference in the azo weight fractions, which are 0.85 in pDR1M and 0.54 in pMNAP. Higher azo content generates larger birefringence val-

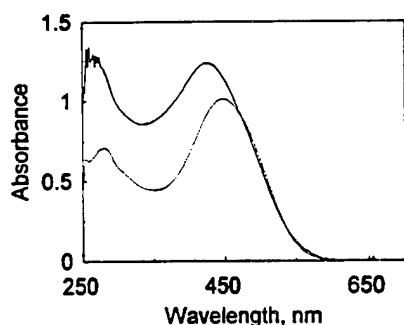


Figure 2. Electronic spectra of pMNAP in DMSO solution (.....) and in film (—).

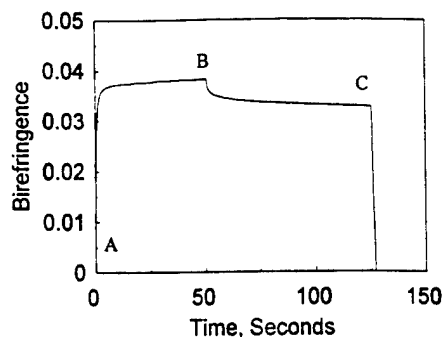


Figure 3. Writing-erasing curve of pMNAP film. At point A the linearly polarized laser (writing beam) is turned on; at point B the writing beam is turned off; at point C the circularly polarized laser (erasing beam) is turned on.

ues if the azo chromophores have the same contribution to birefringence. The second factor may be the difference in mobility of the two kinds of azo groups. The azo groups in pDR1M or pDR1A are linked to the backbone by one bond. In pMNAP the connection to the backbone is through two chemical bonds, thus restricting the motion of azo groups. Therefore the ability to move the azo groups may be lower in pMNAP than in pDR1M or pDR1A. The third may be the difference between the absorbance maximum wavelength and the writing laser wavelength ($\lambda_{\text{max}} = 425$ nm for pMNAP and $\lambda_{\text{max}} = 458$ nm for pDR1M; $\lambda_{\text{laser}} = 488$ nm). In addition to these, pMNAP has a higher T_g (152°C) than both pDR1A (92°C)² and pDR1M (129°C),² which certainly reduces the mobility of the azo groups at room temperature, at which the laser operates.

In order to understand the writing process the birefringence growth can be fitted with the following biexponential equation⁷

$$\Delta n = A \cdot \{1 - \exp(-k_a \cdot t)\} + B \cdot \{1 - \exp(-k_b \cdot t)\} \quad (1)$$

where Δn represents the birefringence achieved at time t , k_a and k_b are the time constants for writing, and A and B are constants. The sum of A and B represents the maximum induced birefringence, and the normalized A and B (A_n and B_n , respectively) will represent the contribution of each of the two terms to the induced birefringence. The experimental points and the fitted curve are shown in Figure 4, and the fitting parameters are listed in Table I. The two terms in eq. (2) mean that the whole writing process can be approximated by two kinds of motions, one faster—associated with the side groups,

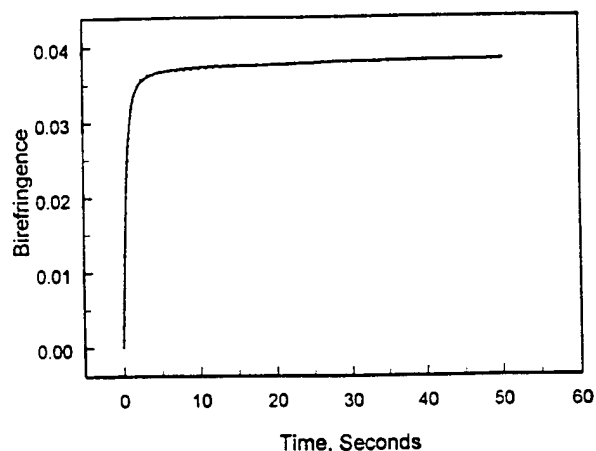


Figure 4. The experimental and biexponential fitted writing curve: Solid line: fitted curve; dots: experimental points.

and the other slower—associated with the main chain motions.⁷

The relaxation curve can similarly be fitted with a biexponential equation as follows⁷

$$\Delta n_r = C \cdot \exp(-k_c \cdot t) + D \cdot \exp(-k_d \cdot t) + E \quad (2)$$

where Δn_r is the relaxed birefringence at time t after turning off the writing laser, k_c and k_d represent the time constants of the birefringence relaxation for the two kinds of motion, C and D are the constants relating to the contribution of the two motions to the birefringence relaxation and E is the final birefringence independent on time. The sum of normalized C and D (C_n and D_n , respectively) describes the fraction of birefringence lost and the normalized E (E_n) represents the fraction of stable birefringence. The fitting results are listed in Table II. It is acceptable to compare these results with those of pDR1M obtained in similar conditions with another wavelength laser ($\lambda = 514 \text{ nm}$)⁷ since the laser is off in the relaxation process. It is clear that the relaxation rates of pMNAP are lower than those of pDR1M shown in Table II. This can be attributed to their differences in structures. The benzene rings at both ends of azo group in pDR1M may rotate

Table I. Writing Rates and Normalized Constants for Eq.(1)

k_w, s^{-1}	k_r, s^{-1}	A_n^a	B_n^a
1.68 ± 0.02	0.08 ± 0.01	0.94 ± 0.05	0.06 ± 0.01

$$^a A_n = A/(A + B); B_n = B/(A + B).$$

Table II. Relaxation Rates and Normalized Constants for Eq. (2)

	pMNAP	pDR1M ⁷
k_c, s^{-1}	0.69 ± 0.01	1.90 ± 0.06
k_d, s^{-1}	0.04 ± 0.01	0.11 ± 0.01
C_n^a	0.06 ± 0.01	0.075
D_n^a	0.06 ± 0.01	0.078
E_n^a	0.88 ± 0.01	0.846

$$^a C_n = C/(C + D + E); D_n = D/(C + D + E); E_n = E/(C + D + E).$$

freely around the azo bond since there is a spacer between the azo chromophore and the backbone. One of the benzene rings of pMNAP is blocked by the main chain so that its freedom of rotation around the azo bond is reduced. As a result of this, the induced alignment level of azo groups in pMNAP relaxes at a slower rate than in pDR1M.

The films were written and erased at variable temperatures up to T_g . It was found that the saturated birefringence level decreases when the temperature increases (Table III). However about 20% of the value obtained at room temperature is still achievable at 138°C , very close to the T_g . The writing and relaxation curves obtained at variable temperatures were also fitted with eq. (1) and eq. (2) and the fitting results are summarized in Table IV. The fraction of stable birefringence (E_n) for pMNAP is 0.88, which is better than that for pDR1M ($E_n = 0.846$)⁷ at room temperature. It is as high as ca. 0.5 even at 138°C .

As showed in Table IV the contribution of the fast process (represented by A_n) apparently decreases when the temperature increases from room temperature to about 60°C and then becomes constant. This may suggest that the contribution of the slow motion (represented by B_n) becomes more important at higher temperatures, even though the fast motion is still the main contributor. Similarly, k_c

Table III. Optical-Induced Birefringence at Variable Temperatures

Temperature ($^\circ\text{C}$)	Saturated Birefringence Level	Relaxed Birefringence Level
23	0.029	0.026
53	0.026	0.022
80	0.022	0.016
105	0.017	0.012
138	0.011	0.006

Table IV. Relaxation Rates and Normalized Constants at Variable Temperatures for Eqs. (1) and (2)

Temperature, °C	k_a, s^{-1}	k_b, s^{-1}	A_n^a	B_n^a	E_n^a
23	1.09	0.024	0.96	0.04	0.90
53	0.69	0.077	0.73	0.27	0.84
80	0.55	0.078	0.70	0.30	0.73
105	0.42	0.058	0.69	0.31	0.69
138	0.04	0.055	0.72	0.28	0.53

$$^a A_n = A/(A + B); B_n = B/(A + B); E_n = E/(C + D + E).$$

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decreases and k_b remains about constant when the temperature increases, which means the fast process slows down with the temperature. This probably is because the thermal motion of the side chains at higher temperature helps in randomizing the photoinduced orientation. This is the same kind of temperature effect found for pDR1M film under irradiation with different laser powers.¹⁹

When the film is cooled down to room temperature, the original level of birefringence can be regained. These results suggest that the birefringence lost at high temperature is directly related to the motions taking place in the polymer film.

CONCLUSIONS

pMNAP shows adequate writing properties and a fairly stable birefringence level especially at high temperatures. The structure of the azo groups prevents them from aligning freely, so that the birefringence achieved is limited to about 0.04 at room temperature. The fact that pMNAP decomposes at about 160°C prevents its use as a material for optical storage.

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