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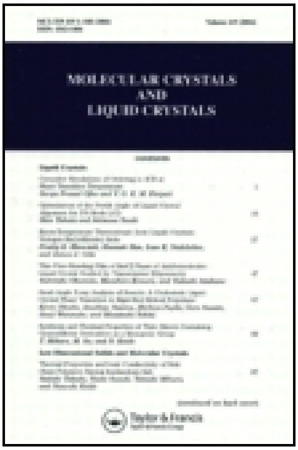

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Photoinduced Birefringence and Optical Rotation on Achiral Azobenzene Copolymer

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Photoinduced birefringence and photoinduced optical rotation has been investigated on poly{4-[2-(methacryloyloxy)ethyloxy-4′-cyanoazobenzene]-co-4-[[2-(methacryloyloxy) ethyloxy]-2-methyl-4-(phenylazo)]azobenzene} (PCDY50). Originating in a good optical response of cyanoazobenzene side-chain and large birefringence of long π-conjugated side chains, a fairly large photoinduced birefringence (0.28) and photoinduced optical rotation (41°/μm) could be observed. Some applications utilizing these superior photoresponsive properties of PCDY50 have been suggested and demonstrated.

Keywords: achiral azobenzene polymer; photo-alignment; photoinduced birefringence; photoinduced chirality; photoinduced optical rotation

INTRODUCTION

It is well known that azobenzene materials respond to light and take a specific molecular orientation state, which depends on the condition of

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irradiated light. The irradiation of linear polarized light is the simplest case. In this case, azobenzene molecules preferably re-orient to the direction perpendicular to the electric field of excitation beam. The mechanism of this phenomenon can be explained as following: when excitation beam is irradiated to an azobenzene film, trans–cis photoisomerization takes place on each molecule and the cis-form immediately relaxes back to rod-like trans-form. Thus the trans–cis–trans photoisomerization cycle continues as long as the excitation beam irradiated. However, if the trans-form azobenzene molecules once align perpendicular to the electric field of excitation beam, that molecules are excluded from the continuous photoisomerization cycle because the molecules do not absorb incoming light any more. As a result, the population of the molecules aligned to perpendicular to the electric field of the excitation beam increases according to the irradiation time. Finally, macroscopic birefringence is brought about in the irradiated area. This phenomenon is called as photo-alignment of azobenzene (or photoinduced birefringence) and is quite promising for rewritable optical memory application.

On the other hand, in case the elliptically polarized light (EPL) is irradiated, the azobenzene molecules take other specific orientation state. The formation of a specific orientation state can be observed as an appearance of optical rotation and circular dichroism just after the EPL irradiation even in "achiral" azobenzene materials and even the initial state is completely isotropic. This is called as photoinduced chirality. One of the possible explanations on the induction of photoinduced chirality in "achiral" material is originated in photofabrication of helical structure in a long-range (or short-range) order [1–4]. In other word, the azobenzene molecules align to one direction in the plane perpendicular to the light propagation direction and the director in the plane gradually changes its direction with a tiny twist along the light propagation.

So far, it has been reported that typical azobenzene polymers exhibit photoinduced birefringence of $0.05 \sim 0.20$ [5] and photoinduced optical rotation of $\sim 15^{\circ}/\mu\text{m}$ [1–3]. On these circumstances, we have designed new photoresponsive copolymers (PCDY's) that consists of cyanoazobenzene and long π-conjugated side chains in order to improve those optical performances [6]. The former is introduced as photo-alignment trigger with good optical response and the latter is for large birefringence, high order parameter and good stability of aligned state. As one can easily imagine, since the optical performances also depend on its copolymerization ratio, several copolymers with different copolymerization ratio have been synthesized and compared [7]. From the previous work, it was found that the optical

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properties of PCDY's depend on the copolymerzation ratio of two azobenzene monomers. The tendency is not monotonously. Consequently, 1:1 copolymer of 4-[2-(methacryloyloxy)ethyloxy-4′-cyanoazobenzene] and 4-[[2-(methacryloyloxy)ethyloxy]-2-methyl-4-(phenylazo)]azobenzene (PCDY50) exhibited best performance among many PCDY's with different coplymerization ratio. Thus, in this paper, we have investigated photoinduced birefringence and photoinduced optical rotation on the PCDY50, and referred some possible applications.

EXPERIMENT

The copolymer consists of cyanoazobenzene and 4-[4-(phenylazo) phenylazo]-*o*-cresol at the molar ratio of 1:1 (PCDY50) has been synthesized by polymerization of 4-[2-(methacryloyloxy)ethyloxy-4′-cyanoazobenzene] and 4-[[2-(methacryloyloxy)ethyloxy]-2-methyl-4-(phenylazo)] azobenzene. Amorphous thin films of about 1 μm-thick with good optical quality were obtained by spin coating from 5 wt% of dichloromethane solution filtered by 0.45 μm pore membrane. Spin coating was performed in the dried nitrogen atmosphere at room temperature.

In order to investigate photoinduced birefringence and photoinduced optical rotation on the PCDY50 films, a pump-probe optical configuration was employed. Pump and beam were CW laser beams, which diameters were 3 and 1 mm, respectively. The pump beam was incident normally on the sample and the probe beam was at small angle with respect to the pump beam. The elliptic state of pump and probe beams were controlled by a linear polarizer and a variable waveplate. The wavelength of the pump beam was varied in the range of 405 to 514.5 nm, and the probe beam was 633 nm that is out of the absorption band of the PCDY50.

For the photoinduced birefringence measurements, polarization direction of the linearly polarized probe beam was set to vertical and also the linearly polarized pump beam was set to -45° with respect to the probe beam. For the photoinduced optical rotation measurements, the pump beam was adjusted to be EPL with desirable ellipticity whose principal axis was set to the vertical. The principal axis of the elliptically polarized probe beam was selected to vertical (the same azimuthal angle with the pump beam) or horizontal direction (the difference in azimuthal angle with respect to the pump beam is 90°). In both experiments, the polarization state of the probe beam transmitted through the azobenzene film was measured by a polarimeter, which can measure four Stokes parameters of the light simultaneously. The value of photoinduced birefringence, ellipticity change and azimuthal rotation were calculated by observed Stokes parameters.

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RESULTS AND DISCUSSION

Figure 1 shows the response of photoinduced birefringence dynamics on PCDY50. It was found that the value increased quickly and saturated within 70 sec. The maximum value was 0.244 for the excitation with a linearly polarized beam of 488 nm at 1 W/cm^2. For holographic memory application, it is desirable that the product value of birefringence multiplied by film thickness [μm], which is called as dynamic range, is large enough. In the PDCY50, the birefringence value is so large that it is very easy to realize few tens of dynamic range with the film less than 100 μm. This result is attributed to an ingenious combination of good photoresponse of cyanoazobenzene moiety and a large molecular birefringence (highly anisotropic structure) of 4-[4-(phenylazo)phenylazo]-*o*-cresol moiety. Moreover, it is note worthy that there was no relaxation on the photoinduced birefringence after turning off the pump beam. The glass transition temperature of the PCDY50 is higher by 20°C than that of conventional methacrylate-based azopolymers that have been widely investigated for memory application, so that the PCDY50 is expected to have better archival life than the conventional methacrylate-based azopolymers. Moreover,

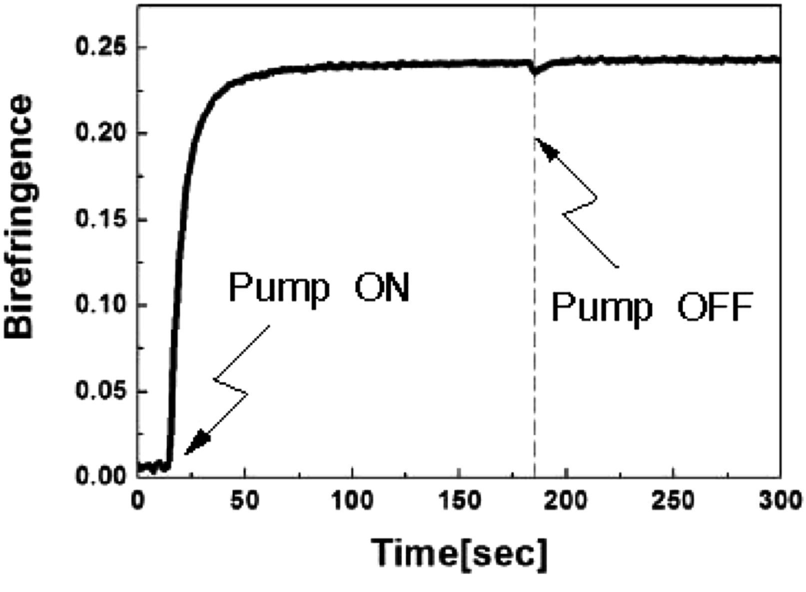

FIGURE 1 Photoinduced birefringence dynamics of the PCDY50 during excitation and after turns off the beam. The excitation starts at 15 sec, and terminated at 180 sec.

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this material is readily soluble for organic solvents and one can make a high quality film. Thus, an application for rewritable holographic memory and/or other optical addressable devices is anticipated.

Figure 2(a) is a reconstructed image of a data recorded on the PCDY50 film by Fourier holography. One can superimpose other image [Fig. 2(b)] by overwriting a data on the recorded spot [Fig. 2(c)]. The recorded data can erase by a single beam exposure. After the optical erasure, other data can be recorded again at the same position on the film. Figure 2(d) is the reconstructed image of the data recorded after the optical erasure of the previously recorded data [Fig. 2(c)].

Figure 3 shows a dependence of photoinduced birefringence of the PCDY50 on pump beam wavelength. It was found that 457.9 nm excitation induced the highest value (0.28). However, this tendency was

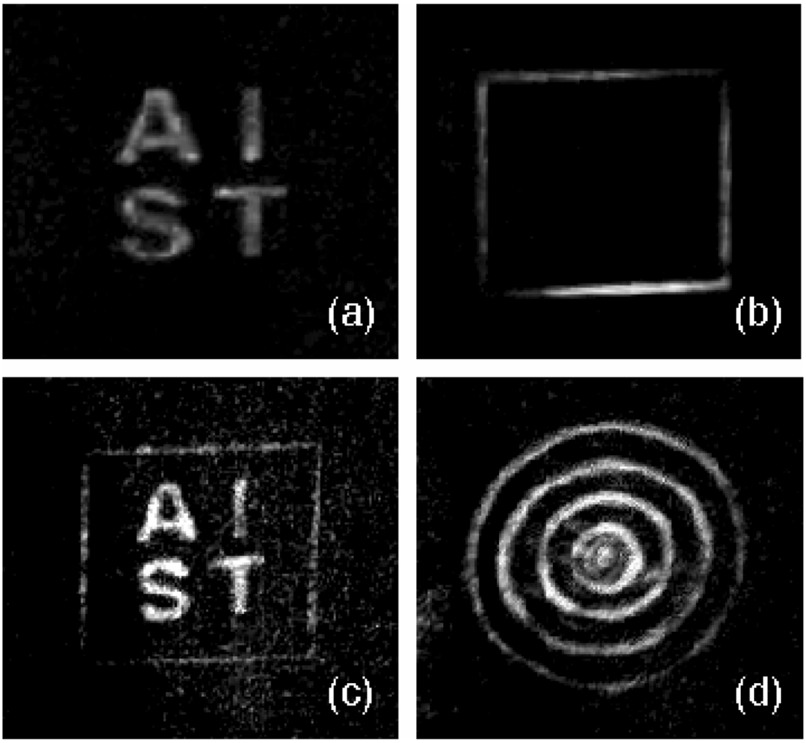

FIGURE 2 Demonstration of rewritable holographic data storage on the PCDY50. Images were recorded by Fourier hologram. (a) Characters of “AIST”, (b) a rectangle, (c) the rectangle image was overwrited on the image of “AIST”, and (d) circles recorded on the same spot after optical erasure of the previous image.

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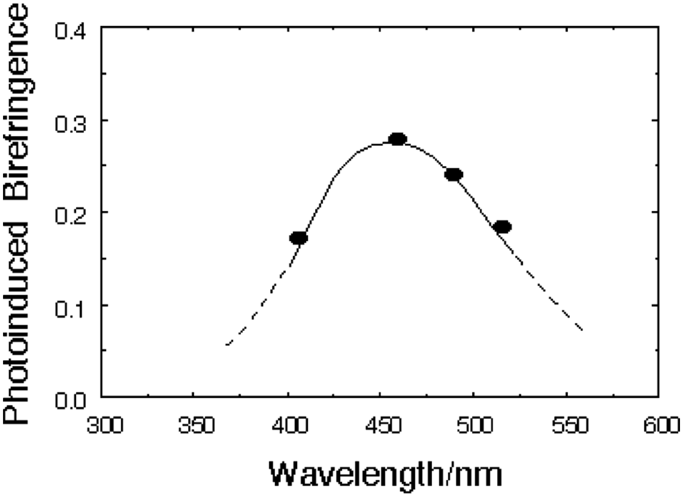

FIGURE 3 Wavelength dependence of photoindued birefringence on the PCDY50.

not simply correlated with a dispersion of absorption coefficient of the PCDY50. Then, the absorption spectrum of the PCDY50 was deconvoluted into two Gaussian functions as shown in Figure 4. (Spectral deconvolution was performed in regard to the photonenergy, but not to the wavelength of the light.) The inset of the figure is the replotted data of photoinduced birefringence shown in Figure 3, and a solid line in the inset is a Gaussian fitting curve. (Fitting was also performed as a function of the photonenergy.) As a result, it was indicated that the deconvoluted band located on long wavelength side corresponds to the wavelength dispersion of photoinduced birefringence though the Gausian width and peak position does not coincide precisely.

According to the result of quantum chemistry calculation with INDO/2 parameter, the band on the absorption tail is originated in the electronic transitions of two azo functional groups (−N=N−bonding). This result provides a significant viewpoint for elucidating photoisomerization and optical alignment mechanism of the PCDY50, and for effective usage of the material. One should take into account this result on designing azobenzene molecules for further development.

When we irradiated azobenzene polymer film with elliptically polarized light (EPL) instead of linearly polarized light, photoinduced optical rotation was observed nevertheless the material is achiral. In the PCDY50 film, the difference between the ellipticity of the transmitted EPL and that of incident EPL (pump beam) is little, but just

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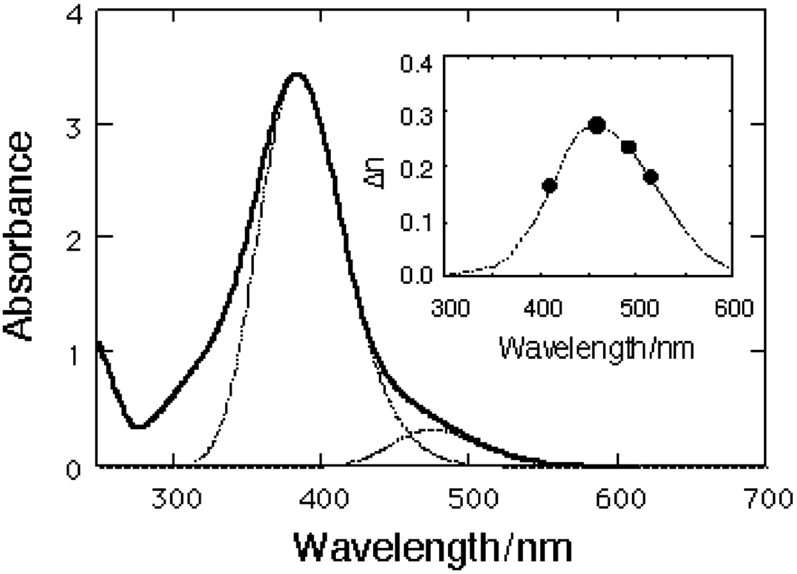

FIGURE 4 Deconvolution of absorption spectrum of the PCDY50 and relation between the photoinduced birefringence.

a rotation of the principal axis of the EPL was brought about. (Strictly, the ellipticity change of the transmitted beam is not zero. It might be attributed to the difference in the direction of birefringence and the direction perpendicular to the principle axis of EPL, which does not satisfy the waveguide condition for the incident light.) We have already reported that the photoinduced optical rotation of the PCDY50 film depends on excitation conditions, i.e., wavelength, intensity and ellipticity of the pump beam and the optimized condition for the PCDY50 was 457.9 nm, 0.4 W/cm^2 and ellipticity $= -0.5$ [8]. On the optimized condition, a fairly large optical rotation of 41°/μm was observed. This means that a 2.2 μm-thick film of the PCDY50 is affordable to give 90° optical rotation. Thus, practical applications for photoaddressable spatial light modulators, photo-tunable waveplates (birefringent retarder, optical rotator etc.) circular dichroic plates are anticipated. The large optical rotation can be attributed to high photoresponsive property and well-aligned state of azobenzene moieties as was revealed on the photoinduced birefringence measurement.

It was already described that the ellipticity change of the excitation light is quite small in the excitation by EPL (blue ~ green) although large optical rotation comes about. However, if we input an additional

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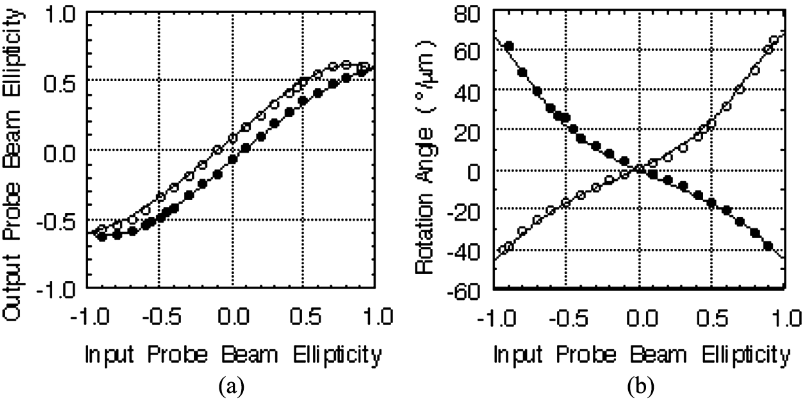
EPL with the wavelength other than that of the excitation EPL, the feature mentioned above is not maintained any more. Namely, both the rotation of the principal axis and the modulation of the ellipticity of the EPL will occur simultaneously in general. For example, in the case that we irradiated the PCDY50 film with the beam of 488 nm, 0.4 W/cm^2 and ellipticity $= -0.2$, the probe beam of He–Ne laser (633 nm) with -0.7 ellipticity (azimuthal angle was equal to that of the pump beam) will be changed to ellipticity $= -0.6$ and affected optical rotation of 40°/μm.

Figure 5 explains the details how the He–Ne probe beam affects optical modulation under the condition mentioned above. In order to use the PCDY50 for practical phototunable waveplates, appropriate conditions for incident He–Ne beam should be satisfied. The conditions for an optical rotator and for an ellipticity modulator are called as invariant ellipticity state (IES) and invariant azimuth state (IAS), respectively. In general, an elliptic state of the light can be expressed by complex polarization variable (χ) that is a function of the azimuth (θ) and ellipticity angle (ε). Especially, in the circular vector basis, the complex polarization variable χ can be represented as $\chi = \tan(\varepsilon + \pi/4) \times \exp(-i \cdot 2\theta) =$ Real $[\chi]$+Imaginary $[\chi]$. According to the experimental data that obtained by the excitation with 488 nm beam at 0.4 W/cm^2 and ellipticity $= -0.2$, IES and IAS were solved and plotted as functions of real and imaginary part of the χ in Figure 6. (It should be noticed that the IES



(a) (b)

FIGURE 5 Relationship between the ellipticity of input probe beam and transmitted probe beam (633 nm). The ellipticity of excitation beam was -0.2. Solid and open circle correspond to the case the probe beam with the same azimuthal angle and with difference in azimuthal angle of 90° to the excitation beam, respectively.

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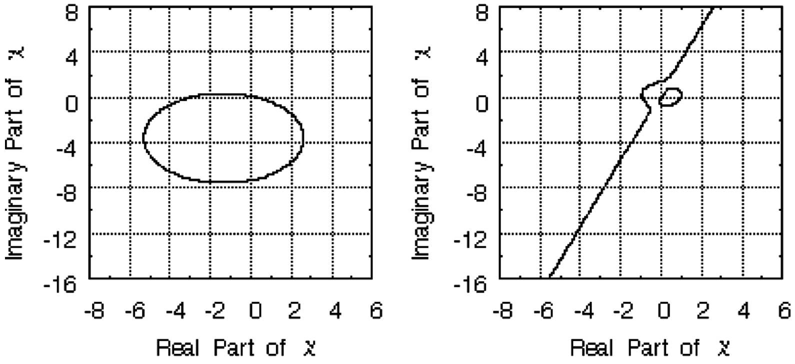

(a) (b)

FIGURE 6 IES and IAS condition concerning the complex variable χ for the 0.8 μm PCDY50 film excited by 488 nm beam at 0.4 W/cm^2 and ellipticity = −0.2.

and IAS conditions shown in Figure 6 is applicable only for the film with 0.8 μm. The results will be different on other thickness films because IES and IAS conditions depend on experimental conditions including the film thickness.) Therefore, the PCDY50 film just acts as the optical rotator or

TABLE 1 Special Conditions for Useful Optical Functions

Elliptic state of the 633 nm probe beam Optical function	Ellipticity (Input)	Azimuth (Input) [°]
+45° rotator	−0.715	–14.011
+90° rotator	−0.783	−36.054
+135° rotator	−0.705	−58.796
−45° rotator	0.692	32.179
−90° rotator	0.772	54.821
−135° rotator	0.700	77.422
Right circular polarization generator (Ellipticity = +1)	0.584	55.323
Left circular polarization generator (Ellipticity = −1)	−0.605	−35.851
+0.5 ellipticity generator	0.872	−35.882
−0.5 ellipticity generator	−0.853	52.814
Linear polarization generator	−0.235	42.281
Eigenvalue 1*	0.0189	−80.223
Eigenvalue 2*	−0.0464	8.737

*Neither the ellipticity nor the azimuth change at eigenvalues.

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the ellipticity modulator for the He–Ne beam that satisfying the elliptic conditions illustrated in the figure. For example, the input He–Ne beam of ellipticity $= -0.783$ and azimuth $= -36.716^\circ$ changes to ellipticity $= -0.783$ and azimuth $= 53.284^\circ$ ($+90^\circ$ rotator condition). Similarly, the beam of ellipticity $= 0.584$ and azimuth $= 55.323^\circ$ changes to ellipticity $=$ 1.000 and azimuth $= 55.323^\circ$ (Right circular polarization generator condition). Typical useful functions can be achieved at the conditions as listed in Table 1.

CONCLUSION

The PCDY50 that newly developed azobenzene side chain-type copolymer exhibited best performance among the copolymers we have investigated, i.e., photoinduced birefringence of 0.28 (irradiated at 457.9 nm, $1\,\mathrm{W/cm^2}$ and ellipticity $= 0.0$) and photoinduced optical rotation of $41^\circ/\mu\mathrm{m}$ (irradiated at 457.9 nm, $0.4\,\mathrm{W/cm^2}$ and ellipticity $= -0.5$). These observed values are fairly large comparing to those ever reported. It is considered that these superior optical properties are attributed to the introduction of large linear birefringent moiety bearing a good affinity with cyanoazobenzene moiety at the appropriate composition ratio (1:1). Concerning the dependence of photoinduced birefringence on the excitation beam wavelength, it was found that the absorption band locates on the absorption tail plays an important role in the PCDY50. Superior new polymers might be designed by taking into account this aspect. Thus, further investigation on azobenzene copolymers for practical application as rewritable holographic recording medium or tunable optics such as photo-addressable spatial light modulators, photo-tunable waveplates (birefringent retarder, optical rotator etc.) and circular dichroic plates are greatly anticipated.

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