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Improvement in linear and nonlinear optical-properties by blending poly(*N*-vinyl-2-pyrrolidone) with an electro-optic polymer

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Abstract

Poly(*N*-vinyl-2-pyrrolidone) (PVP) has been blended with a urethane–urea copolymer (UU); this resulting electro-optic polymer was thought to improve the linear and nonlinear optical properties. Transparent films without scattering were obtained from the mixed solutions of PVP and UU with a wide mixture ratio. The refractive indices and absorption coefficients of the films decreased with the nonlinear optical (NLO) chromophore concentration. The optical nonlinearity, which was evaluated by the *d*-coefficient for second harmonic generation, was enhanced by blending 10–20 w/w% PVP with UU in spite of a decrease in the NLO chromophore concentration. No noticeable lowering of the temporal stability of the nonlinearity was observed in the blended film containing 10–20 w/w% PVP. The improvement induced by the addition of a small amount of PVP could not be explained by the interaction between the NLO chromophore and PVP but between UU and PVP. The blended films containing 10–20 w/w% PVP showed an improvement in temporal stability at 100°C by additional heating during corona poling. The blending of polysulfone (PSF) with UU was examined, and the blended film containing 10 w/w% PSF showed no observable change regarding the *d*-coefficient and its temporal stability.

Keywords: Nonlinear optics; Blend; Poly(*N*-vinyl-2-pyrrolidone)

1. Introduction

Numbers of electro-optic (EO) polymers have been investigated to fabricate a high-performance light modulator due to their advantages, such as large optical nonlinearity, fast response time, and low dielectric constant [1–6]. EO polymers attracted our attention because of their diversity of molecular structure and processability for multilayer structures.

However, several problems with EO polymers still remain to be solved for a fabricating optical devices and assembling the devices into a system: for example, unstable optical nonlinearity, insufficient transparency, weak mechanical properties, and controllability of the refractive index. The decrease in nonlinearity is caused mainly by the orientation relaxation of an azo-containing nonlinear optical (NLO) chromophore. Several approaches were carried out to improve the relaxation by introducing either cross-linking [7] or hydrogen bonds [8]. The transparency of the film is improved not only by the decrease in the absorption coefficient but also by the reduction of fluctuation of the refractive index. Therefore, the uniformity of the film is an important factor. The weak mechanical property is sometimes caused by low molecular weight so that voids and cracks in the film are generated during the preparation of the film. These defects also decrease the transparency by scattering the light. The waveguide structure is essential for an optical device, and it requires at least a few μm in thickness to be defined. Therefore, sufficient mechanical properties are also important for an EO polymer. Although there were many EO polymers with high optical nonlinearity, all of them could not be the candidates for application due to their weak mechanical properties caused by low molecular weight. The fine control of refractive index is also demanded to define a single mode waveguide, which is always used for an EO light modulator. Furthermore, the coupling between the optical fiber and the waveguide of a device demands a low refractive index of the core.

We have proposed blending another polymer with the EO polymer to solve the above problems on the whole. The controllability of refractive index and the reinforcement of mechanical properties would be expected mainly by blending another polymer. However, the optical nonlinearity and temporal stability could be decreased simultaneously. In this paper, we have examined the changes in the linear and nonlinear optical properties to confirm the possibility of a blending effect.

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Poly(*N*-vinyl-2-pyrrolidone) (PVP), which has a wide variety of commercial applications [9], was selected as a blending reagent with the EO polymer. PVP is soluble in polar solvents and interacts with proton-donating materials through hydrogen bonding. Therefore, PVP has been shown to exhibit miscibility with many proton-donating polymers [10–12]. On the other hand, improvement of transparency for a sol–gel film has been reported using PVP [13]. In this report, the thermal cross-linking characteristic was also indicated. These properties of PVP could be expected for the improvement of optical characteristics: transparency, controllability of the refractive index and temporal stability of nonlinearity. A urethane–urea copolymer (UU) containing azo-derivatives of a nonlinear chromophore was selected as an EO polymer. Although we have already fabricated a light modulator using UU [14], further improvement is expected by blending.

2. Experimental

2.1. Polymers

Polymer 1 (UU): UU containing an azo-chromophore (UU) was used as the EO polymer. The synthesis and physical properties of UU were previously reported in the literature in detail [15]. The UU showed a glass transition temperature (T_g) of 145°C measured by a differential scanning calorimeter and has a weight-average molecular weight of 170,000 determined by gel-permeation chromatography using mono-disperse polystyrene as the standard.

Polymer 2 (PVP): PVP purchased from WAKO Chemical was used as blending polymer, which has a molecular weight of 40,000 and a T_g of 163°C.

Polymer 3 (PSF): Polysulfone (PSF) was used as an other blending polymer and showed a T_g of 190°C. PSF was given by Teijin Amoco.

The chemical structures of UU, PVP and PSF are shown in Fig. 1.

2.2. Preparations of films

The films of the blended polymer were spin-coated on a glass substrate from a mixed polymer solution dissolved in pyridine after filtering through a 5 μm filter. The good solubility between UU and PVP was attained over the PVP content from 10 to 50 w/w% so that the obtained films showed an amorphous state without scattering. The blended film of UU and PSF was also obtained as an amorphous film in a same manner. The film thickness was measured with a Sloan Technology DEKTAK II profiler. The films were corona-poled in air using a needle electrode in order to induce optical nonlinearity. In general, the poling was performed under the following conditions: inter-electrode distance, 30 mm; applied voltage, 15 kV; poling temperature, 170°C; poling time, 5 min; cooling time, 20 min; applied voltage during the cooling, 12 kV. In order to promote cross-linking, an additional heat treatment (applied voltage, 12 kV; poling temperature, 170°C; poling time, 60 min) was also carried out before cooling. The blended film of UU and PSF was corona-poled at 190 and 210°C. The temporal stability after poling was examined at 100°C and at room temperature in the atmosphere.

2.3. Measurements of optical properties

Absorption spectra of the films were measured with a Shimazu UV-2100 spectrometer before poling. The refractive indices of the films were also measured ranging from 400 to 830 nm in wavelength by a Rudolph ellipsometer.

The second-order non-linear coefficients (*d*-coefficient) of the corona-poled films were measured by the Maker fringe method using a Continuum NY-81 Nd:YAG laser with an 8 ns width and 10 Hz repetition as a 1064 nm fundamental source. The measurements were carried out

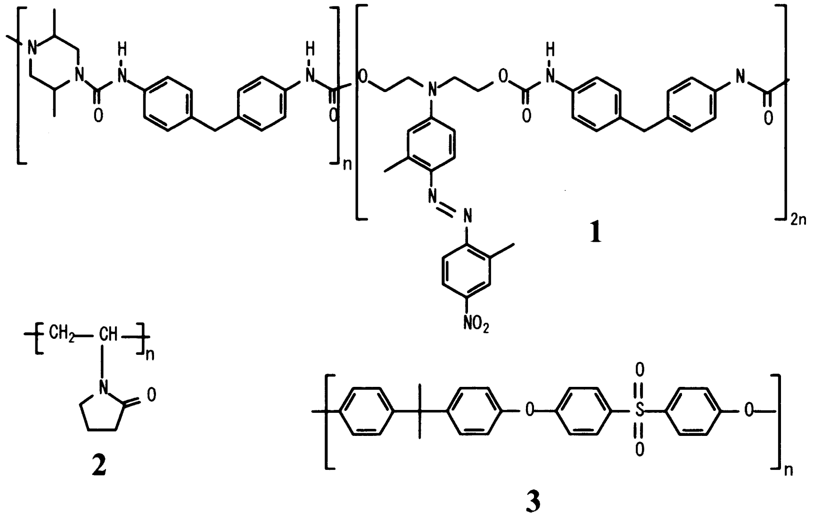

Fig. 1. Chemical structure of polymers.

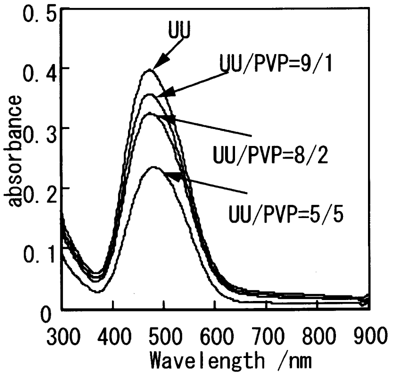

Fig. 2. Absorption spectra of the blended films. The mixture ratios between UU and PVP are indicated in the figure.

by s–p and p–p arrangement. The d_{33} values of the polymers were estimated by the theory of Jerphabnon and Kurtz, [16] assuming $d_{11} = 0.5$ pm/V for quartz. These values were calculated by taking the absorption coefficient of the film [17] at 532 nm and the refractive indices of the films at 1064 and 532 nm.

3. Results and discussion

3.1. Linear optical properties of the UU/PVP films

The transparent films without scattering were obtained from the solutions with a mixture ratio of UU/PVP = 9/1, 8/2, and 5/5. This transparency denotes the totally miscibility of UU/PVP. Fig. 2 shows the absorption spectra of the films. The thickness, absorption peaks ($\lambda_{\max}$) and absorption coefficient at 532 nm are summarized in Table 1. The $\lambda_{\max}$ of the polymer corresponds to the absorption of the NLO chromophore. Although the $\lambda_{\max}$ was slightly shifted to a long wavelength by the addition of a small amount of PVP, the $\lambda_{\max}$ of UU/PVP = 5/5 was markedly shifted. The shift indicates interaction between the NLO chromophore and PVP as observed from the solution. The absorption coefficient decreased with the PVP content, which corresponds to the NLO chromophore content. The decreased coefficient would also contribute to the decline of the propagation loss for the waveguide in the transparent region.

Table 1
Optical properties of the UU film and blended films.

Sample	Thickness (μm)	$\lambda_{\max}$ (nm)	ϵ (μm^{-1})[a]	n_{532}[b]	n_{1064}[c]
UU	0.10	474	6.54	1.91	1.66
UU/PVP = 9/1	0.11	475	5.42	1.87	1.66
UU/PVP = 8/2	0.11	475.5	5.04	1.81	1.65
UU/PVP = 5/5	0.11	484	3.79	1.70	1.60

[a] Absorption coefficient at 532 nm.
[b] Refractive index at 532 nm.
[c] Refractive index at 1064 nm.

Table 2
d-coefficients of the UU film and blended films shortly after poling

Sample	d_{33}[a] (pm/V)	d_{33}[b] (pm/V)
UU	103	–
UU/PVP = 9/1	126	90
UU/PVP = 8/2	109	61
UU/PVP = 5/5	33	29

[a] Obtained under the normal poling conditions described in the text.
[b] Obtained from the samples involved with the additional post heat treatment during poling (applied voltage:12 kV, poling time 60 min).

Fig. 3 shows the refractive index in the blended films as a function of wavelength. The refractive index decreased with the chromophore content as well as the absorption coefficient. The Sellmeir equation [18] was used to estimate the refractive indices at long wavelength by fitting in the transparent region ranging from 630 to 830 nm. The refractive indices measured at 532 nm and the calculated indices at 1064 nm are also summarized in Table 1. A lower refractive index at long wavelength and controllability have been attained by blending the PVP.

3.2. Nonlinear optical property of the UU/PVP film

The *d*-coefficients obtained from a second harmonic generation (SHG) measurement are summarized in Table 2. The *d*-coefficients in the left column were obtained under the normal poling conditions. In spite of a decrease in the chromophore content, two kinds of blended films, UU/PVP = 9/1 and 8/2, show a higher *d*-coefficient than the UU film. The increase in optical nonlinearity and decrease in the refractive index are useful in device applications. On the contrary, the UU/PVP = 5/5 showed a lower *d*-coefficient than that calculated from the decrease in the NLO chromophore.

The optical nonlinearity of a polymer is determined by the environment on the NLO chromophore, such as the content, the local field factor, hyperpolarizability (β), and the orientation distribution. The chromophore content decreases with the introduction of PVP. The decrease in the local field factor was suggested by the decrease in the

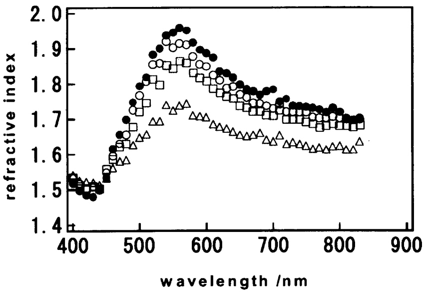

Fig. 3. Refractive indices of the blended films. Solid circles show the indices of the UU film. Open circles, squares and triangles show the indices of the blend films of UU/PVP = 9/1, UU/PVP = 8/2, and UU/PVP = 5/5, respectively.

refractive index. These two factors raise no optical nonlinearity. On the other hand, the increase in β is also expected due to the decrease in excitation energy as shown in the peak shift. β was estimated by a two-level model [19]. Only a few % increase in β was estimated from the decrease in the excitation energy. Therefore, about a 30% increase in the *d*-coefficient would be explained by the higher orientation distribution.

The shift in the $\lambda_{\max}$ of UU/PVP = 5/5 shows that a large amount of PVP affected the interaction between the NLO chromophore and PVP. The *d*-coefficient of PMMA including 10 w/w% NLO molecules (4-(*N*-2-hydroxyethyl-*N*-ethyl)amino-4′-nitroazobenzene: DR1) was measured and was determined to be 1 pm/V. The interaction between the PVP and the NLO chromophore would not improve the orientation. Therefore, we considered that a small amount of PVP affected the main chain of UU at elevated temperature like a plasticizer. The flexible chain, low molecular weight and hydrogen bonding may change the viscosity of UU.

3.3. Relaxation of orientation

Fig. 4 plots the relative change in the *d*-coefficient as a function of leaving time at room temperature. No noticeable difference in relaxation behavior was observed between the UU film and the blended samples of 9/1 and 8/2. These samples maintained a *d*-coefficient of 90% after 900 h. On the contrary, the blended film of 5/5 showed a slightly worse temporal stability.

Fig. 5 shows the relative changes in *d*-coefficient when treated at 100°C. The blended films of 9/1 and 8/2 also show the same relaxation behavior in comparison with UU, and the film of 5/5 shows worse relaxation behavior. Adding a small amount of PVP into the NLO polymer was useful for the enhancement of nonlinearity. Because the initial *d*-coefficients of the blended films of 9/1 and 8/2 were higher than the UU film, the blended films are superior to the UU film in device applications. It has been ascertained that blending of a small amount of PVP with an EO polymer improves linear and nonlinear optical properties without a change in temporal stability.

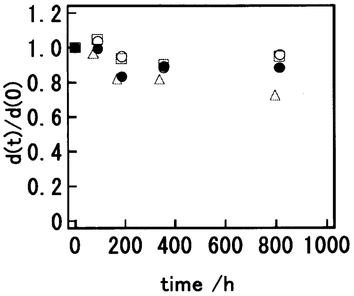

Fig. 4. Changes in the d-coefficient at room temperature as a function of time. The vertical axis shows the ratio of the *d*-coefficient to that obtained shortly after the corona poling. Solid circles show the results obtained from UU film. Open circles, squares and triangles show the results obtained from the blended films of UU/PVP = 9/1, UU/PVP = 8/2, and UU/PVP = 5/5, respectively.

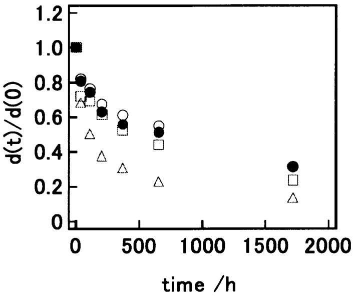

Fig. 5. Changes in the *d*-coefficient at 100°C as a function of time. Marks are identical with those shown in Fig. 4.

3.4. Blending PSF with UU

We also considered that blending a high T_g polymer with EO polymer could improve their properties for the same reason mentioned in the introduction. PSF was chosen because of a high T_g and good solubility with UU.

The film was also obtained from a mixed solution of the UU and PSF and showed the same transparency as the UU polymer without scattering. The absorption coefficient was decreased with the increasing the content of PSF, and no peak shift of $\lambda_{\max}$ was observed. Because PSF shows a T_g of 190°C, the corona poling was performed at 190 and 210°C. A relatively low *d*-coefficient was obtained from the film poled at 210°C. The NLO chromophore could be pyrolyzed at elevated temperature. Because blending of the high T_g polymer requires corona poling at an elevated temperature, degradation of the NLO chromophore should be taken into account. The *d*-coefficients of UU/PSF = 9/1 and 8/2 shortly after 190°C poling were 104 and 64 pm/V, respectively. The film of UU/PSF = 9/1 showed a slight enhancement of nonlinearity. On the contrary, the film of UU/PSF = 8/2 showed a lower *d*-coefficient in comparison to UU/PVP = 8/2. Effectiveness of the improvement in nonlinearity in the blending could depend on the chemical structure of the blended polymer and their quantities. It is

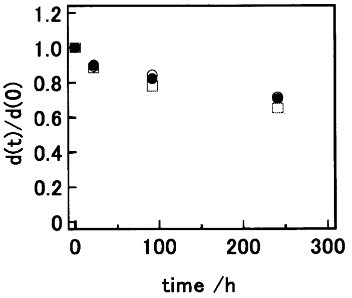

Fig. 6. Changes in the *d*-coefficient at 100°C as a function of time. Solid circles show the results obtained from the UU film. Open circles and squares show the results obtained from the blended films of UU/PSF = 9/1, and UU/PSF = 8/2, respectively.

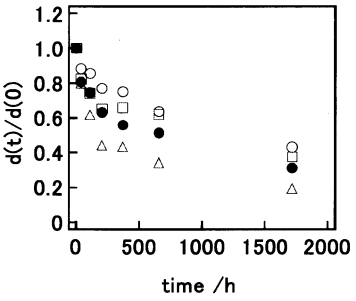

Fig. 7. Changes in the d-coefficient at 100°C as a function of time. All the blended films except the UU film involved the post heat treatment during the poling. Marks are identical with those shown in Fig. 4.

indicated that the interaction between the blending reagent and the EO polymer is important for obtaining the blending effect.

The relaxation experiments at 100°C were also performed and the results are shown in Fig. 6. No noticeable effect of blending on the improvement in relaxation was observed. No effect of blending the high T_g polymer was observed.

3.5. Post heat treatment during the poling

The PVP could cause cross-linking [13], which could improve the temporal stability of nonlinearity. Post heat treatment during the poling was examined to confirm the improvement in stability.

The *d*-coefficients in the right column in Table 2 were obtained from the sample treated by post heating in addition to the normal poling. These *d*-coefficients decreased with decreasing NLO chromophore content. The *d*-coefficient after additional heat treatment showed a low value in comparison with that obtained from general poling. The molecular relaxation could be caused during the poling at elevated temperature and the applied voltage was low under additional poling; therefore, the *d*-coefficient could decrease after additional poling.

Fig. 7 also shows the decrease in the *d*-coefficient at 100°C. The films obtained from the post heat treatment were compared. The films of UU/PVP = 9/1 and 8/2 showed an improvement in relaxation both by introducing the PVP and by the heat treatment during the poling.

We examined the solubility of the blended films after heat treatment. The films treated at 150°C for 1–30 h, however, were dissolved in pyridine and showed no noticeable change in their infrared spectrum. Therefore, no cross-linking could have occurred. The effect of physical aging on the improvement in temporal stability of the *d*-coefficient was reported [20] and was explained by the change in free volume. In our cases, the same effect is considered to improve the temporal stability, which is especially effective due to the flexible main chain of PVP.

4. Conclusions

Blending a small amount of PVP with an EO polymer has brought about an increase in the d-coefficient without a change in temporal stability. We have shown the blending method to be useful for improvement of the linear and nonlinear optical properties. Besides PVP, PSF was also useful as a blending reagent.

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