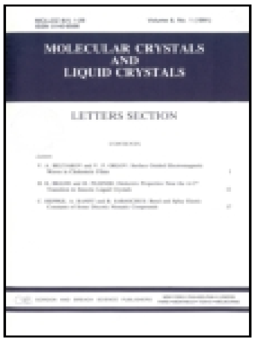

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Properties of Some Polarized Chromophores in Polyvinylpyrrolidone

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*Poor miscibility of highly polarized chromophores to polymer matrices is a crucial issue for EO polymer development. By using poly(*N*-vinylpyrrolidone) (PVP) as a matrix polymer, we were able to prepare the uniform film containing ammonium-borate type zwitterions or Disperse Red 1 (DR1). For zwitterions, corona poling was unsuccessful probably because of hygroscopic property of PVP and/or strong intermolecular interaction to form the antiparallel dimers. For DR1, we found apparent color change originated from the H-aggregate formation assisted by moisture, which is usable to detect humidity. On the other hand, a passivation layer is necessary to use PVP for the EO applications.*

Keywords EO chromophore; zwitterion; azo dye; polymer dispersion; poled polymer

1. Introduction

The development of high performance electrooptic (EO) devices is one of the important research subjects in the field of optical communication due to pressing demands for ultrafast and high-capacity data processing. Organic polymer materials are promising for EO applications because of their large optical nonlinearities, low dielectric constants effective for an ultrafast response, and good processability to fabricate the devices based on the optical waveguides [1]. The simple EO polymers, especially for the R & D purposes, are composed of a matrix polymer and a dispersed EO chromophore with the large first hyperpolarizability (β) [2,3]. Noncentrosymmetric structures of the polymer systems are prepared by the electrical poling. Thus, large dipole moments (μs) should also be provided in the chromophores. Namely, large $\mu\beta$ values are required for the EO chromophores. However, when the chromophores are polarized, their solubilities to the common volatile organic solvents such as chloroform and tetrahydrofuran generally decrease. On the other hand, *N*,*N*-dimethylformamide (DMF) is a better solvent for highly polarized chromophores. However, poly(methyl methacrylate) (PMMA) as a typical optical polymer is not so soluble in DMF, and alternative polymers are necessary. From this view point,

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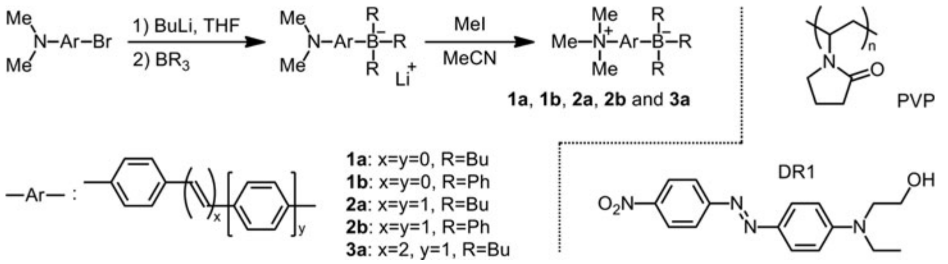

Figure 1. Chemical structures of zwitterions prepared in this study, DR1 and PVP. Synthesis scheme of the zwitterions is also shown.

poly(*N*-vinylpyrrolidone) (PVP in Figure 1) is a promising matrix polymer because of its amorphous feature and high solubility in DMF. However, PVP has rarely been considered for nonlinear optical polymers [4] and we examined it in this study.

For highly polarized chromophores, we selected zwitterions. Disperse Red 1 (DR1 in Figure 1) [2] was used as a reference. From the basic consideration, positive and negative charge centers of the chromophores are better to be separated with a long distance to increase the μ values. In this sense, zwitterions have suitable chemical structures. Especially, zwitterions, in which positive and negative charge centers are isolated from the conjugation system, are interesting species. For example, ammonium and borate groups can be cation and anion centers, which can attract and repel electrons, respectively, in the π-conjugation system connected to them. Thus, zwitterions with ammonium and borate groups at both ends of the π-conjugation systems were selected as appropriate model compounds with large $\mu\beta$ [5]. However, they seemed to have low miscibility with common organic solvents and polymers.

In the present study, several ammonium-borate-type zwitterions were synthesized, and they or DR1 was dispersed in PVP. The properties of these chromophore-doped PVP films were investigated.

2. Experimental

Zwitterions were synthesized according to the reaction scheme in Figure 1. As an example, **3a** was obtained as follows: To 1.64 g of 4-(4-bromophenyl)-1,3-butadienyl-(*N*,*N*-dimethyl)aniline (5 mmol), 300 mL of anhydrous THF was added under a nitrogen atmosphere and the solution was cooled to –78°C with stirring. To the solution, 3.1 mL of 1.6 mol/L *n*-butyllithium hexane solution (5 mmol) was added dropwise. After addition completion, the reaction mixture was stirred for 1.5 h. Then, 5 mL of 1.0 mol/L tributylborane THF solution (5 mmol) was added dropwise to the mixture. It was warmed up to ambient temperature to stir further for 2 h after addition completion. Solvent in the reaction mixture was removed in vacuo, and 75 mL of acetonitrile and 2.5 mL of iodomethane (40 mmol) were added to the residue. After stirring the mixture overnight, the solvent was evaporated and water was added. The insoluble portion was collected by suction filtration and washed with ethanol. The collected solid was recrystallized from acetone-ethanol mixture to afford 0.64 g of **3a** (29%) as yellow crystals. IR (KBr) 2948, 2865, 2832, 2784, 1619, 1575, 1461, 1417, 1367, 1286, 1193, 1141, 989, 933, 844, 798 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6, δ) 7.88 (d, $J = 9.1$ Hz, 2H), 7.70 (d, $J = 9.1$ Hz, 2H), 7.25 (d, $J = 8.3$ Hz, 2H), 7.23 (dd, $J = 16.0, 10.5$ Hz, 1H), 7.04 (d, $J = 8.3$ Hz, 2H), 6.85 (dd, $J = 15.6, 10.5$ Hz,

Table 1. Melting point and absorption peak at the longest wavelength of zwitterions

Compound	M.p.[a] / °C	λ_{max} / nm (ε_{max} / Lmol^{-1}cm^{-1})	Solvent[b]
1a	218	241 (6.3×10^3)	MeOH
1b	365 (dec.)	–	
2a	248 (dec.)	352 (3.1×10^4)	MeCN
2b	289 (dec.)	337 (3.3×10^4)	DMF
3a	264 (dec.)	373 (4.0×10^4)	MeCN

[a] Decomposition is indicated by dec.
[b] Used for absorption measurements.

1H), 6.70 (d, $J = 15.6$ Hz, 1H), 6.64 (d, $J = 16.0$ Hz, 1H), 3.58 (s, 9H), 1.11 (m, 6H), 0.89 (m, 6H), 0.75 (t, $J = 7.2$ Hz, 9H), 0.12 (broad m, 6H)

PVP with M_n of 5.5×10^4 and DR1 were purchased from Sigma-Aldrich. Chromophore-doped polymer films were prepared by the spin-coating method, in which DMF and chloroform were used as solvents for zwitterions and DR1, respectively. The films of **1a** for absorption spectral measurements were obtained on quartz substrates while the other samples were prepared on glass slides. Corona poling experiments were performed using a high-voltage source (Touwa Keisoku AKT-015KP). The spin-coated films on glass slides were placed on a copper-plate cathode, and a tungsten-needle anode was fixed 1 cm above of the film surface.

3. Results and Discussion

Table 1 summarizes melting points and absorption maximum wavelengths (λ_{max}s) of zwitterions synthesized. They are thermally stable up to more than 200°C. Among them, **1a**, **2a** and **3a** with a tributylborate group were soluble in DMF. However, **1b** and **2b** with a triphenylborate group were hardly dissolved and not appropriate for the spin-coated films. The potential of the zwitterions were able to be confirmed by calculation using MOPAC PM5. The μ and β values of **2a** were obtained to be 42.2 D and 269×10^{-30} esu, respectively. Since μ and β values of DR1 were calculated to be 8.3 D and 31×10^{-30} esu, respectively, $\mu\beta$ of **2a** is fourty-four times larger than that of DR1. For **1a** and **2a**, the uniformly doped PVP films were able to be prepared up to the chromophore content of 40 wt% and 20 wt%, respectively, to the host polymer. The λ_{max}s of **1a** and **2a** in PVP were measured at about 250 nm and 358 nm, respectively. They are similar to those in solution. Figure 2 (a) shows variation of absorbance at λ_{max} and glass transition temperature (T_g) of the PVP films depending on the content of **2a**. The absorbance linearly increased up to 20 wt% indicating that the chromophore dispersion state was uniform within this concentration range. Similar tendency was also observed for **1a** up to 40 wt%. However, the absorption increase regarding the chromophore concentration (ΔA) reduced at high chromophore content. i.e., ΔA from 20 to 40 wt% was 64% of ΔA from 0 to 20 wt%. The T_g of PVP was reported to be 155°C [6] and gradually lowered by adding the chromophore. The T_gs of the PVP films containing 20 wt% of **1a** and **2a** were 132 °C and 119°C, respectively. Corona poling was performed for the PVP film doped by 10 wt% of **2a** at 130°C for 2 h with 12 kV/cm. After poling, UV absorption of the film decreased because of orientation of the chromophore molecules perpendicular to the substrate. Post-annealing at 130°C for 1 h resulted in recovery of the absorption (Figure 2 (b)). This kind of absorption change is often observed in the poled

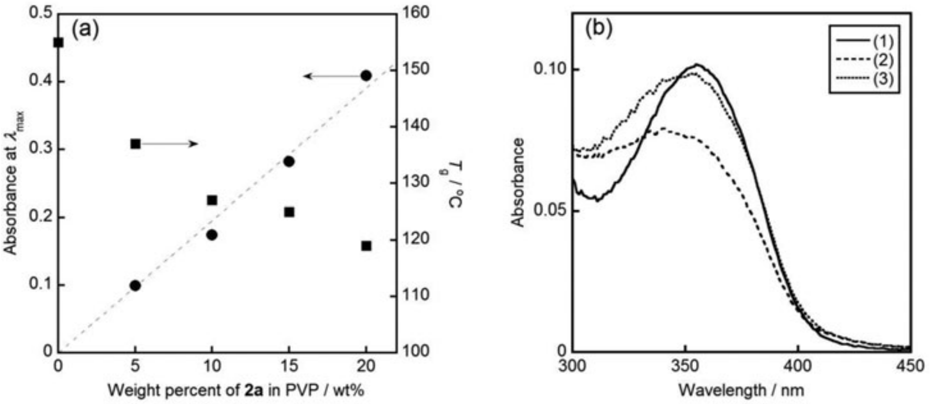

Figure 2. (a) Absorbance at 358 nm (●) and T_g of the PVP films depending on content of **2a** (■). (b) Absorption spectra of a PVP film of **2a** (10 wt%) before and after poling: (1) As prepared, (2) after corona poling and (3) after corona poling followed by heating at about 130°C for 1 h.

films. However, second-harmonic generation (SHG) from the film was not observed at all. Although PVP is hygroscopic as mentioned later, water was removed at poling temperature and did not affect the poling efficiency. However, readsorption of atmospheric water may cause reorientation of the chromophores. Other plausible explanation is that the zwitterions may form the antiparallel dimers in the films due to the large molecular dipole moment. When the antiparallel dimers are formed, the molecular dipole moments are canceled and effective polar orientation of the zwitterions in the polymer matrices cannot be achieved. If so, molecular design to dissociate the aggregated zwitterions such as introduction of bulky substituents should be considered. On the other hand, nonpolar orientation of dimers originated from the induced dipole moments may be possible since there is dielectric anisotropy even in the dimer. This may be the reason why the poled films showed absorption decrease (Figure 2 (b)) but no SHG was observed.

For the DR1-PVP films, we accidentally found a sudden color change of the film from clear red to thin orange by moisture as shown in Figure 3 (a). DR1 in PVP showed absorption maximum at 516 nm. However, this absorption band diminished by moisture and a new sharp peak appeared at 402 nm. When the absorption band of dyes becomes sharp and shifts to shorter wavelength compared with the original monomeric absorption band, it is usually attributed to formation of H-aggregates, in which dye molecules are aligned with π-π stacking in the parallel manner. Some azobenzene derivatives are known to form the H-aggregates in certain conditions [7,8]. For DR1, the H-aggregates was only reported in the thin film prepared by the physical vapor deposition method [9] and quite rare. By varying humidity, we found that this transformation was prominent when relative humidity was more than 50% at ambient temperature. When the film was heated at 90°C, the absorption band at 516 nm recovered and sharp absorption at 402 nm decreased as shown in Figure 3 (a). After heating for 6 h, the spectrum almost coincided with that of the original state. This indicates that the spectral change is reversible. Although vapors of hexane, ethyl acetate, and acetone were exposed to the DR1-PVP films, no spectral change was observed. In the case of methanol vapor, the film was dissolved by condensed methanol but the spectral shape of the film was not changed. As a reference, we also prepared DR1-PMMA films. The absorption band was observed at 492 nm. When the film was exposed to

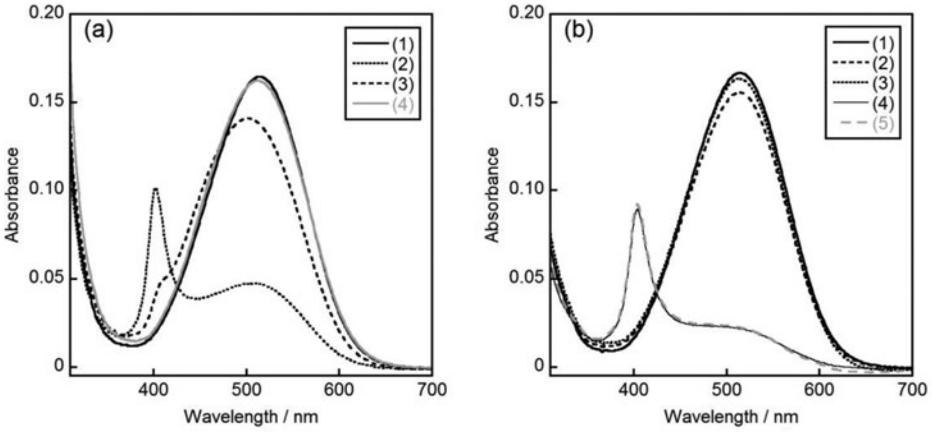

Figure 3. Absorption spectral changes of a PVP film containing DR1 (5 wt%). (a) The effect of moisture and post heating: (1) As prepared, (2) after exposure to moisture, and heating at about 85°C for (3) 10 min and (4) 6 h, respectively, after exposure to moisture. (b) Angular dependence of absorbance: (1) As prepared, (2) and (3) after corona poling and (4) and (5) after corona poling followed by moisture treatment. Incident angles of the probe beam were 0º for (1), (2) and (4) and 30º for (3) and (5).

moisture, no spectral change was detected. Namely, important factors for DR1 H-aggregate formation were not only water existence but also use of PVP matrix.

Since the aggregated state may show enhanced NLO properties, poling of the H-aggregated DR1 seemed to be interesting. However, unfortunately, T_g of DR1-containing PVP was determined to be 90°C and the H-aggregates of DR1 easily dissociated at this temperature. Thus, moisture treatment of poled DR1-PVP films was investigated. After poling at 90°C for 1 h with 15 kV/cm, the absorption band of DR1 decreased when the incident beam angle is 0º. However, when the spectrum of the same poled polymer was recorded at incident angle of 30º, absorbance increased (compare curves (2) and (3) in Figure 3 (b)) indicating normal orientation of the chromophore [10]. Then, we treated the poled film with moisture and found that there were no difference between the spectra measured at incident angles of 0º and 30º (see almost overlapped curves of (4) and (5) in Figure 3 (b)). From this result, DR1 molecules must be aligned in the parallel or antiparallel manner in the H-aggregates but orientation of the aggregates was randomized during the aggregate formation assisted by moisture.

4. Conclusion

We succeeded to prepare uniform polymer films of highly polarized chromophores such as ammonium-borate-type zwitterions by using PVP. However, PVP has a hygroscopic property and a passivation layer for the PVP film is necessary in the EO applications to avoid water adsorption from a humid atmosphere. Although the orientation parallel to the electric field of the zwitterions in PVP was observed in the poling condition, no SHG was observed. This seemed to be caused by hygroscopic properties of PVP and/or strong dipolar intermolecular interaction among the zwitterions to diminish the large dipole moment. In addition, the borate groups as model anion centers were reported to be thermally and photochemically unstable in some conditions [11,12], and other anion centers should be introduced to zwitterions for the applications.

On the other hand, moisture sensitivity of PVP induces interesting color changes of DR1 in the film. DR1 dispersed in PVP formed the H-aggregates when the film was exposed to moisture. Upon heating, disaggregation occurred and the film recovered to the original state. Other organic vapors did not assist aggregate formation. Thus, the DR1-PVP films can be used for simple visual moisture sensors. However, for the EO applications, a passivation layer is required to keep the performance of the PVP-based polymers.

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