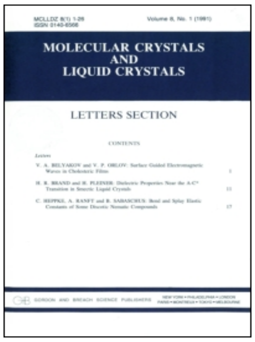

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Substituent modification of electro-optic chromophores with 4-cyano-5-dicyanomethylene-2,5-dihydro-1*H*-pyrrol-2-one as an acceptor

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ABSTRACT
Electro-optic chromophores with 4-cyano-5-dicyanomethylene-2,5-dihydro-1*H*-pyrrol-2-one (CDCOP) and aniline moieties as an acceptor and a donor, respectively, were synthesized with modification of three substituents, among which two were attached to the aniline moiety (R) and one was introduced to the CDCOP ring (R′). Butyl and hexyl groups were introduced as R and R′, and higher melting points were observed when R and R′ were the same. For the chromophore fixation, thermal crosslinking based on cyanate trimerization was performed. The chromophore with cyanate moiety in R′ was combined with bisphenol A dicyanate, and the thermal chromophore fixation was confirmed with almost no chromophore degradation.

KEYWORDS
EO chromophore; polymer dispersion; cyanate; polycyanurate; poled polymer

1. Introduction

Electro-optic (EO) devices are expected to be used for ultrafast optical information processing [1]. One of the promising materials for the EO devices is polymers with chromophores composed of a π-conjugation system terminated with electron accepting and donating groups. 4-Cyano-5-dicyanomethylene-2,5-dihydro-1*H*-pyrrol-2-one (or 4-cyano-5-dicyanomethylene-2-oxo-3-pyrroline (CDCOP)) is a strong acceptor, and CDCOP derivatives combined with a donor have been known as a series of dyes more than fifty years ago [2, 3]. Recently, they are received as useful EO chromophores [4–6]. In order to obtain high-performance EO polymers, the chromophores should be molecularly dispersed in the matrix polymer for efficient electrical poling although chromophores often form aggregates in the polymer [7]. Also, the polar structure generated by electrical poling should be fixed to avoid temporal relaxation.

In this study, CDCOP derivatives with an aniline moiety were synthesized with modification in the alkyl substituents and these properties were investigated. A cyanate group, which is thermally trimerized to form cyanurate (Figure 1) [8, 9], was also introduced as one of the substituents to fix the chromophores in the polymer matrix of polycyanurate (PCN).

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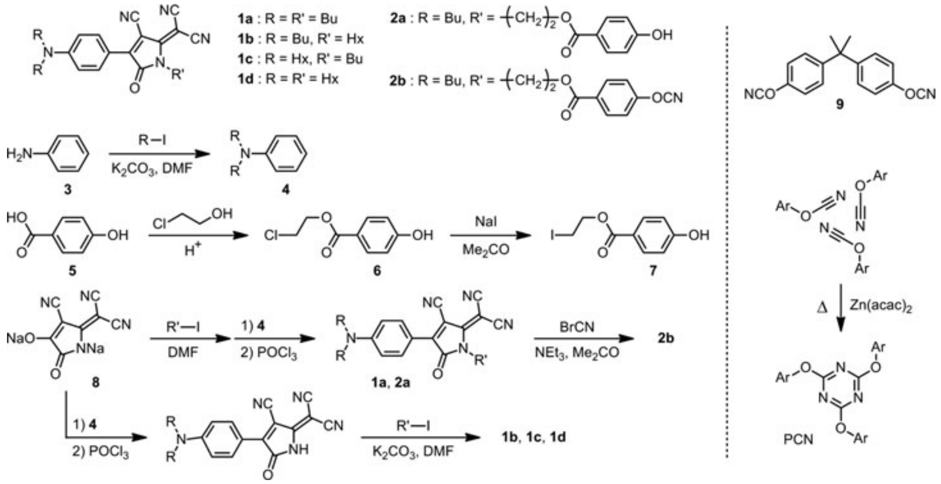

Figure 1. Chemical structures and synthesis schemes of CDCOP derivatives and polycyanurate (PCN). Hx and Ar indicate hexyl and aryl groups, respectively.

2. Experimental

Chromophores **1** and **2** with a CDCOP moiety were synthesized according to the reaction scheme in Figure 1. *N,N*-Dialkylaniline derivatives **4** were prepared by heating the mixture containing aniline **3**, alkyl iodide and potassium carbonate in DMF. Ester **6** was obtained by esterification of 4-hydroxybenzoic acid **5** in ethylene chlorohydrin with sulfuric acid as a catalyst. Halogen exchange of **6** from chlorine to iodine was performed by sodium iodide in acetone to give **7**. A one-pot reaction including *N*-alkylation of **8** and coupling between the resulting *N*-alkyl compound and **4** gave CDCOP derivatives **1a** and **2a**. For **1b**–**1d**, coupling reaction between aniline and CDCOP acceptor **8** and *N*-alkylation were performed stepwise. The chemical structures of the products were mainly identified by ^{1}H- and ^{13}C-NMR spectra. Synthesis procedures of **2a** and **2b** are described below.

To 0.23 g (1 mmol) of **8** [10] in DMF (2 mL), 0.32 g (1.1 mmol) of **7** was added and the mixture was stirred at 60 °C for 2 days. The mixture was cooled by a salt-ice bath and 0.23 g (1.1 mmol) of *N,N*-dibutylaniline was added. Next, 0.28 mL (3 mmol) of phosphoryl chloride was added dropwise, and the mixture was stirred for 1 h after addition completion. The bath was removed and the mixture was further stirred for 4 h at ambient temperature. Then, water (600 mL) was poured into the mixture and stirring was continued overnight. The mixture was filtered and the filtered solid was purified using a column chromatography (silica gel, chloroform-ethyl acetate (9:1)) to give 0.25 g (46%) of **2a** as a violet solid: Mp 156 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 0.99 (6H, t, $J = 7.3$ Hz), 1.40 (4H, tq, $J = 7.3, 7.3$ Hz), 1.65 (4H, tt, $J = 8.0, 7.3$ Hz), 3.45 (4H, t, $J = 8.0$ Hz), 4.55 (4H, s), 6.10 (1H, brs), 6.73 (2H, d, $J = 9.4$ Hz), 6.85 (2H, d, $J = 8.7$ Hz), 7.88 (2H, d, $J = 8.7$ Hz), 8.47 (2H, d, $J = 9.4$ Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, δ) 13.81, 20.19, 29.63, 40.64, 51.38, 59.37, 61.77, 93.69, 110.71, 113.00, 113.43, 113.92, 115.43, 115.95, 121.54, 132.04, 133.89, 141.55, 153.38, 156.00, 160.41, 165.95, 167.38; IR (KBr) 3400, 2958, 2931, 2871, 2219, 1725, 1606, 1550, 1268, 1230, 1205, 1164, 1110, 1093 cm^{-1}.

To 0.35 g (0.65 mmol) of **2a** in anhydrous acetone (4.0 mL) cooled by a salt-ice bath, 0.16 g (1.5 mmol) of cyanogen bromide in anhydrous acetone (1 mL) was added at once. Triethylamine (1 mL) was added dropwise, and the mixture was stirred for 2 h at ambient temperature. The precipitates were collected by filtration and purified by column chromatography (silica gel, chloroform-ethyl acetate (9:1)) to give 0.13 g (36%) of **2b**: Mp 158 °C; ^{1}H-NMR

(400 MHz, $CDCl_3$, δ) 1.00 (6H, t, $J = 7.2$ Hz), 1.41 (4H, tq, $J = 7.5$, 7.2 Hz), 1.66 (4H, tt, $J = 7.7$, 7.5 Hz), 3.46 (4H, t, $J = 7.7$ Hz), 4.57 (2H, t, $J = 4.4$ Hz), 4.63 (2H, t, $J = 4.4$ Hz), 6.74 (2H, d, $J = 9.5$ Hz), 7.36 (2H, d, $J = 9.1$ Hz), 8.11 (2H, d, $J = 9.1$ Hz), 8.49 (2H, d, $J = 9.5$ Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, δ) 13.78, 20.16, 29.60, 40.45, 51.39, 59.43, 62.66, 93.36, 107.75, 111.35, 113.07, 113.47, 113.82, 115.44, 115.89, 128.20, 132.40, 133.80, 141.14, 153.41, 155.69, 155.80, 164.42, 167.44; IR (KBr) 3442, 2960, 2933, 2283, 2258, 2237, 2219, 1731, 1606, 1552, 1504, 1396, 1363, 1205, 1095 cm^{-1}; Found: C, 63.60%; H, 5.86%; N, 11.63%. Calcd for $C_{32}H_{30}N_6O_4$: C, 63.88%; H, 5.86%; N, 11.64%.

Poly(methyl methacrylate) (PMMA, $M_w = 1.2 \times 10^5$, Aldrich) and poly(oxycarbonyloxy-1,4-phenylenecyclohexane-1,1-diyl-1,4-phenylene) (PCZ-300, Mitsubishi Gas Chemical), which is an amorphous polycarbonate, were used as polymer dispersion media of chromophores **1a**–**1d**. Poly(acrylic acid) (PAA, $M_w = 1.0 \times 10^5$, Aldrich) was used to form a passivation layer of the thin films.

Thin films of PCN were obtained as follows. At first, a soluble prepolymer (PP) of PCN was prepared. The mixture of dicyanate **9** (100 mg) and zinc acetylacetonate (ZAA, 0.25 mg) was heated in ethanol at 80 °C for 5 min and the following solvent evaporation gave PP. Then, **1a** or **2b** was mixed to PP in the ratio of 0.1 mmol of the chromophore to 1 g of PP, and ZAA (0.25 wt% to PP) was added. The mixture was dissolved in THF and spin-coated on glass slides. The films were heated at 120 °C for 30 min.

For corona poling, a grounded copper plate was placed on a temperature-controllable heater, and a spin-coated film on a glass slide was put on the plate. A tungsten needle was set 1 cm above the film and a positive voltage was applied.

3. Results and discussion

The melting points of **1a, 1b, 1c** and **1d** were found to be 129 °C, 93 °C, 91 °C and 118 °C, respectively. It is interesting that the chromophores with the same alkyl group as R and R′ have the melting points higher than 118 °C while those with different alkyl groups have lower melting point of around 90 °C. In general, high melting point suggests large intermolecular interaction of the component molecules. In the chromophore dispersion system in polymers, anti-parallel molecular aggregation often becomes a crucial issue to reduce the poling efficiency. Thus, introduction of different alkyl groups to chromophores may diminish intermolecular interaction resulting in one of the good solutions to avoid aggregate formation. In order to investigate the intermolecular interaction of these chromophores, single crystal growth and the crystallographic analyses are in progress.

Figure 2 shows UV-visible spectra of **1a**. Figure 2 (a) is comparison of the spectra in chloroform, PMMA and PCZ-300. The concentration of **1a** was 5 wt% for both polymers. Absorption of these spectra is normalized by absorbance at each maximum. Absorption maximum wavelengths (λ_{max}s) of **1a** in chloroform, PCZ-300 and PMMA were 658 nm, 652 nm and 637 nm, respectively. Although the λ_{max}s are different among them, this fact seems to be caused by difference in the surrounding media of the chromophores. Meanwhile, widths of the absorption bands are not so different between chloroform solution and polymer mixtures. The λ_{max}s of the CDCOP derivatives **1b**–**1d** with different alkyl groups in PMMA with 5 wt% concentration were almost the same as those of **1a**. These results indicate that the chromophores are nearly dispersed in the molecular state in these polymers.

Figure 2 (b) shows UV-visible absorption spectra of **1a** in PMMA (10 wt%). For the as-prepared spin-coated film, the λ_{max} is slightly shifted to shorter wavelength by 4 nm compared with that of 5 wt% dispersion, but the chromophore aggregation seemed to be

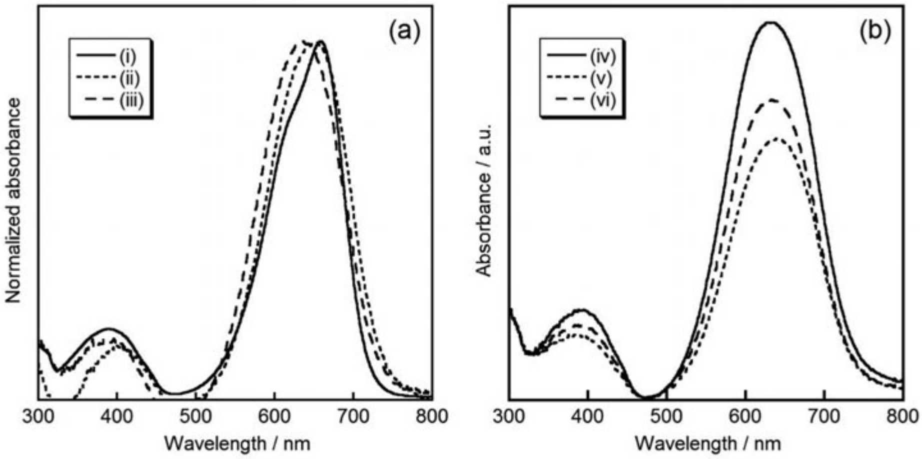

Figure 2. UV-visible spectra of **1a**. The spectra in Figure (a) were measured in (i) chloroform solution, (ii) PCZ-300 and (iii) PMMA and were normalized by absorbance at λ_{max}. Chromophore concentration of **1a** in PCZ-300 and PMMA was 5 wt%. Figure (b) is the spectra of **1a** in PMMA (10 wt%) for corona poling: (iv) just after spin-coating, (v) after corona poling (see text in detail) and (vi) after post-heating.

not so prominent from the absorption shift. After corona poling applying 6 kV/cm at 110 °C for 10 min, the absorbance of the absorption band became small (Figure 2 (iv) → (v)). Since absorption increase by post-heating at 110 °C for 10 min was observed (Figure 2 (v) → (vi)), the chromophores in the polymer should be oriented in a polar manner after poling. However, the absorbance did not completely recovered after post-heating indicating that a part of chromophores were degraded during poling process. This damage could be diminished by covering the film by a passivation layer described later.

For **2b** with cyanate group in R′, the thermal behavior was first investigated to know the crosslinking temperature. The solution of **2b**, PP and ZAA for spin-coating was put on an aluminum pan for DSC measurement. As shown in Figure 3 (a), a broad exothermic peak originated from the crosslinking reaction of cyanate trimerization was observed starting from approximately 60 °C. In the measuring condition, the peak was recorded at around 140 °C

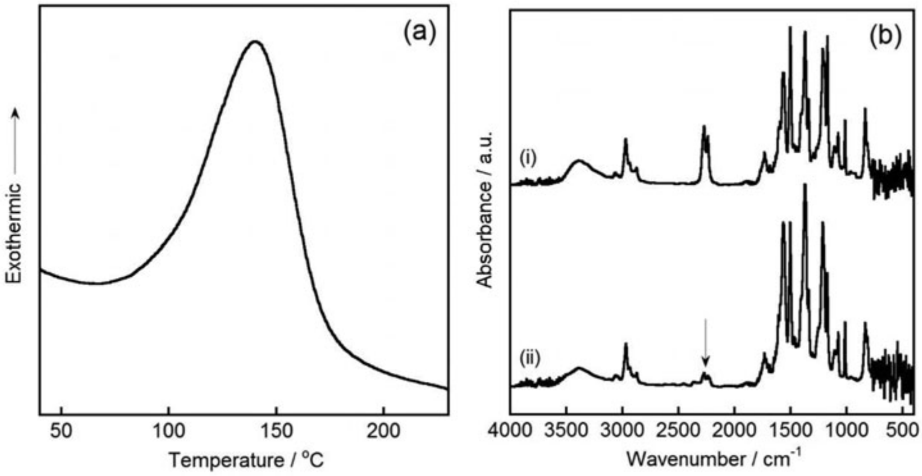

Figure 3. DSC thermogram (a) and FT-IR spectra (b) of the mixture of **2b**, PP and ZAA. In Figure (b), spectrum (i) is for before heating and spectrum (ii) is for after heating at 120 °C for 30 min.

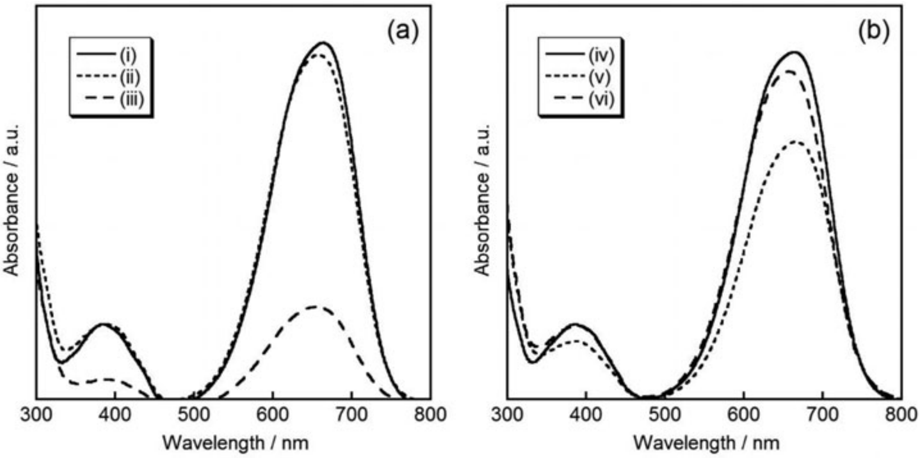

Figure 4. UV-visible spectra of the spin-coated films composed of **2b**, PP and ZAA. Figure (a) is for chromophore extraction by acetone: (i) just after spin-coating, (ii) after heating at 120 °C for 30 min and (iii) after the heat treatment followed by soaking in acetone for 3 min. Figure (b) is for corona poling: (iv) just after spin-coating, (v) after corona poling (see text in detail) and (vi) after post-heating.

and the exothermic reaction ceased at around 200 °C. Thus, the crosslinking reaction of the mixture was conducted at 120 °C, which was included in the exothermic peak range. In the FT-IR spectra, the C≡N stretching vibration peaks at 2237 and 2272 cm^{-1} decreased by heating (Figure 3 (b)). The peak decreasing ratio was almost saturated after heating time of 20 min.

Figure 4 shows UV-visible absorption spectra of spin-coated films containing **2b**, PP and ZAA. The $\lambda_{\max}$ of the film before heating was observed at 665 nm (Figure 4 (i)). After heating at 120 °C for 20 min, the $\lambda_{\max}$ was shifted to 656 nm (Figure 4 (ii)). It should be noted that the absorbance of the chromophore was almost preserved even after the crosslinking reaction in the present case. It is contrastive to acrylate-modified CDCOP derivatives, whose absorption bands degraded during the crosslinking via radical polymerization [6]. When the crosslinked film treated at 120 °C for 30 min was soaked in acetone for 3 min, 31% of the chromophore remained (Figure 4 (iii)). Meanwhile, in the same condition using **1a** instead of **2b**, almost all chromophores were extracted. This large difference is caused by chromophore crosslinking when **2b** was used.

Corona poling was performed for the spin-coated films containing **2b**. When an electric field of 6 kV/cm was applied at 30 °C, absorption degradation due to the sample damage was observed. Thus, PAA dissolved in water (3.3 wt%) was spin-coated on the film as a passivation layer. After drying under reduced pressure, the film did not show degradation by corona poling at 30 °C. Then, corona poling of the film applying the same voltage was conducted with increasing temperature from 60 °C to 180 °C for 15 min followed by decreasing temperature to 40 °C for 5 min. After poling, the absorption band of the chromophore reduced (Figure 4 (iv) → (v)) indicating chromophore orientation perpendicular to the substrate. Since second-harmonic generation (SHG) of the film was observed, the polar structure was also confirmed. However, post-heating at 100 °C for 5 min resulted in absorption recovery (Figure 4 (vi)). From this result, we can conclude that the chromophore was not seriously damaged during the poling process but the polar orientation was instable at high temperatures. The thermal stability of orientation may be improved to some extent by optimizing curing process. However, **2b** is connected only by one arm to a PCN network and the essential solution seems to be more connection points of the chromophore, i.e., introduction of cyanate groups in R.

4. Conclusion

Two series of the CDCOP derivatives were synthesized. For the derivatives with alkyl groups, large melting point difference was found between those of $R = R'$ and those of $R \neq R'$, suggesting different molecular interactions in the crystalline state. On the other hand, these derivatives mixed with 5 wt% concentration in PMMA or PCZ-300 showed the absorption spectra similar to those in solution indicating their molecularly dispersed states in the polymers. For the derivative with a cyanate group in R', fixation of the chromophore was achieved by heating with the dicyanate-based prepolymer. The heating process for crosslinking via cyanate trimerization was found to be useful because of almost no degradation of the chromophore. Since one cyanate group per chromophore was insufficient to maintain the chromophore orientation, introduction of the cyanate group in both R and R' should be worth investigating.

Acknowledgments

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