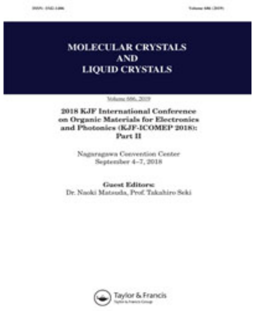
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Substituent engineering of electrooptic chromophores to suppress their aggregation

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ABSTRACT
Chromophores composed of 4-cyano-5-dicyanomethylene-2-oxo-3-pyrroline (CDCOP) and a donor have been synthsized for electrooptic applications. Three substituents of [5-(4-aminophenyl)-2-thienyl]-substituted CDCOP **1** and (4-aminophenyl)-substituted CDCOP **2** were modified to suppress the aggregation for effective poling. To **1**, bulky and branched 2-ethylhexyl groups were introduced instead of linear alkyl groups. Less aggregation was confirmed in the polymer dispersion films, and the corona poling behaviors were examined. To **2**, we introduced norbornyl epoxide groups as bulky and thermally crosslinkable moieties. The aggregation was suppressed as well, and the thermal crosslinking of the epoxide with acid anhydride in the presence of a base was investigated.

KEYWORDS
EO chromophore; polymer dispersion; poled polymer; crosslink

1. Introduction

The first-order electrooptic (EO) effect, which is classified in a second-order nonlinear optical effect, causes refractive index changes of matrials by applying electric field. By using this effect, the devices for optical switching triggered by the electrical modulation have been fabricated. For ultrafast and high-capacity information optical processing in the next generation, EO materials should have low dielectric constants and inorganic materials do not satisfy this point. Meanwhile, organic materials with low dielectric constants can follow high-frequency modulation. In addition, polymers with EO chromophores [1,2] have adventages on processabllity into optical waveguides. For the EO chromophores, thr large first hyperpolarizability (β) as well as the large dipole moment (μ) to align the chromophores in a polar manner by the poling process are required, and various chlomophores have been developed. Since 4-cyano-5-dicyanomethylene-2-oxo-3-pyrroline (CDCOP) is a strong acceptor, its chromophores combined with donors are also good candidates for EO applications [3–10]. On the other hand, their efficient poling is still an unresolved issue. One of the problems is aggregation of the chromophores in the matrix polymers. In the present study, we report substituent engineering

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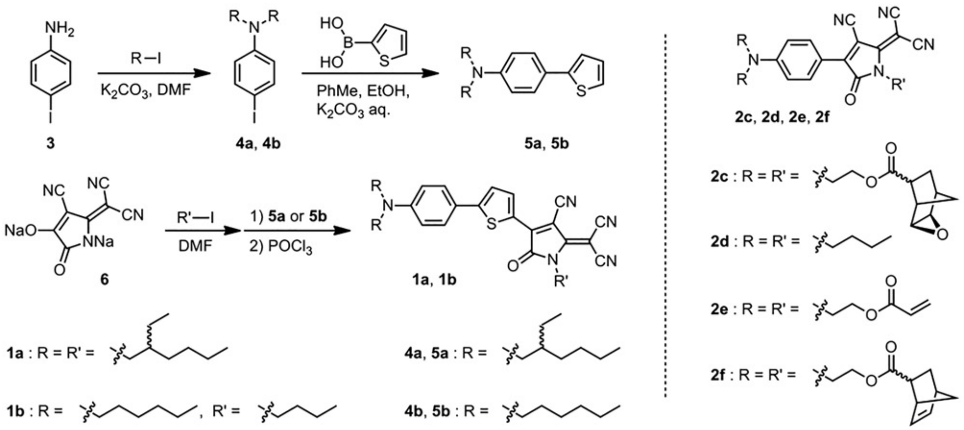

Figure 1. Synthesis scheme of **1** and structures of **2**.

of the CDCOP chromophores for less aggregation. Subsituents of the EO chromophores were converted from simple linear alkyl chains to branched substituents (**1a** in Figure 1) or bulky crosslinkable substituents (**2c** in Figure 1) to suppress aggregation without loosing compatibility with the matrix materials. Their aggregation behaviors were mainly elucidated from the optical properties.

2. Experimental

Synthesis scheme of **1a** and **1b** is shown in Figure 1. Synthesis procedure of **1a** from 4-iodoaniline **3** is described below.

N,*N*-Bis(2-ethylhexyl)-4-iodoaniline **4a**. To a mixture of **3** (3.29 g, 15 mmol) and potassium carbonate (6.22 g, 45 mmol) in DMF (30 mL), 2-ethyl-1-iodohexane (10.8 g, 45 mmol) was added, and the mixture was stirred at 80 °C for 24 h. Then, water was added to the mixture and it was extracted with ethyl acetate-hexane mixture. The combined organic layer was dried over anhydrous sodium sulfate and filtered. Solvent in the filtrate was removed in vacuo, and the residue was purified by column chromatography (silica gel/hexane) to give 1.27 g (19%) of **4a** as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 7.40 (2H, d, $J = 8.1$ Hz), 6.42 (2H, d, $J = 8.1$ Hz), 3.00–3.24 (4H, m), 1.68–1.80 (2H, m), 1.17–1.40 (16H, m), 0.80–0.95 (12H, m);^{13}C-NMR (100 MHz, $CDCl_3$, δ) 147.68, 147.66, 137.41, 114.94, 75.45, 56.24, 36.51, 36.50, 30.60, 30.58, 28.66, 28.64, 23.86, 23.16, 14.07, 10.67, 10.65. Underlined numbers are sets of ^{13}C peaks at the same position in the diastereomers. 2.38 g (48%) of *N*-(2-ethylhexyl)-4-iodoaniline was also obtained as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 7.39 (2H, d, $J = 8.7$ Hz), 6.37 (2H, d, $J = 8.7$ Hz), 3.51 (1H, broad s) 2.96 (2H, d, $J = 6.4$ Hz), 1.53 (1H, m), 1.23–1.43 (8H, m), 0.90 (6H, t, $J = 7.6$ Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, δ) 148.16, 137.67, 114.78, 77.12, 46.82, 38.89, 31.21, 28.91, 24.39, 23.05, 14.07, 10.87.

N,*N*-Bis(2-ethylhexyl)-4-(2-thienyl)aniline **5a**. To 0.37 g (0.32 mmol) of tetrakis(triphenylphosphine)palladium(0) under a nitrogen atmosphere, 1.40 g (3.2 mmol) of **4a** in toluene (15 mL), 0.53 g (4.1 mmol) of 2-thiopheneboronic acid in ethanol (10 mL) and 1.31 g (9.5 mmol) of potassium carbonate in water (3 mL) were added, and the mixture was stirred at 90 °C for 5 h. After solvent evaporation of the mixture in vacuo, brine

(200 mL) was added to the residue and the mixture was extracted with chloroform. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. Solvent in the filtrate was removed in vacuo, and the residue was purified by column chromatography (silica gel, hexane-chloroform (8:2)) to give 0.82 g (65%) of **5a** as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 7.44 (2H, d, $J = 7.4$ Hz), 7.08–7.14 (2H, m), 7.01 (1H, m), 6.64 (2H, d, $J = 7.4$ Hz), 3.15–3.32 (4H, m), 1.80 (2H, m), 1.19–1.44 (16H, m), 0.82–0.96 (12H, m); ^{13}C-NMR (100 MHz, $CDCl_3$, δ) $\underline{147.69,\ 147.67}$, 145.49, 127.74, 126.80, 122.28, 121.43, 120.38, 112.57, 56.35, $\underline{36.75,\ 36.73}$, $\underline{30.65,\ 30.63}$, $\underline{28.69,\ 28.67}$, 23.89, 23.20, 14.10, $\underline{10.69,\ 10.67}$. Underlined numbers are sets of ^{13}C peaks at the same position in the diastereomers.

4-Cyano-5-dicyanomethylene-1-(2-ethylhexyl)-3-(5-(4-(bis(2-ethylhexyl)amino)phenyl)-2-thienyl)-2-oxo-3-pyrroline **1a**. To 4-cyano-5-dicyanomethylene-3-hydroxy-2-oxo-3-pyrroline disodium salt [11] (506 mg, 2.2 mmol) in DMF (5 mL), 581 mg (2.42 mmol) of 2-ethyl-1-iodohexane was added and the mixture was stirred at 60 °C overnight. Then, it was cooled by an ice bath and 799 mg (2.0 mmol) of **5a** was added. Next, 0.5 mL (5.4 mmol) of phosphoryl chloride was added dropwise, and the mixture was further stirred at 0 °C for 1 h and at ambient temperature for 4 h. Water was added to the reaction mixture and the resulting precipitates were filtered. Filtered crude material was purified by column chromatography (silica gel/chloroform) to give **1a** as a dark purple solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 8.56 (1H, d, $J = 4.7$ Hz), 7.66 (2H, d, $J = 9.1$ Hz), 7.44 (1H, d, $J = 4.7$ Hz), 6.72 (2H, d, $J = 9.1$ Hz), 3.93 (2H, d, $J = 7.7$ Hz), 3.24–3.44 (4H, m), 1.79–1.92 (3H, m), 1.17–1.44 (24H, m), 0.84–0.97 (18H, m); ^{13}C-NMR (100 MHz, $CDCl_3$, δ) 166.43, 155.30, 151.13, 140.08, 136.33, 128.74, 124.52, 119.34, 113.18, 113.07, 112.93, 111.56, 92.83, 60.50, 56.36, 45.81, 38.42, 37.27, $\underline{30.62,\ 30.59}$, 29.16, $\underline{28.62,\ 28.60}$, 27.87, 23.90, 23.06, 22.94, $\underline{22.57,\ 22.55}$, $\underline{13.97,\ 13.91}$, $\underline{10.62,\ 10.60}$, 9.95. Underlined numbers are sets of ^{13}C peaks at the same position in the diastereomers.

Compound **1b** with linear alkyl groups was synthsized via the procedure simiar to **1a**. **1b**: Mp. 113 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 8.58 (1H, d, $J = 4.6$ Hz), 7.65 (2H, d, $J = 9.2$ Hz), 7.43 (1H, d, $J = 4.6$ Hz), 6.67 (2H, d, $J = 9.2$ Hz), 4.03 (2H, t, $J = 7.8$ Hz), 3.38 (4H, t, $J = 7.8$ Hz), 1.56–1.72 (6H, m), 1.28–1.46 (14H, m), 0.98 (3H, t, $J = 7.3$ Hz), 0.92 (6H, t, $J = 6.4$ Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, δ) 166.08, 154.85, 150.85, 140.12, 136.04, 128.85, 124.44, 119.01, 113.22, 112.96, 112.09, 111.59, 92.40, 59.78, 51.30, 41.71, 31.57, 31.47, 27.32, 26.70, 22.61, 19.48, 14.01, 13.59.

Compound **2c** with epoxy groups in Figure 1 was synthesized as follows. At first, via the similar procedure to prepare the derivatives of **2d** with butyl groups [3,7–9], **2e** with 2-(acryloyloxy)ethyl groups as R and R' was synthesized. After the Diels-Alder reaction between **2e** and cyclopentadiene, **2f** whose substituents were terminated by a norbornene moiety was obtained. Finaly, C = C bonds of the norbornene moieties of **2f** were epoxydized by *m*-chloroperbenzoic acid. **2c**: ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 8.46 (2H, d, $J = 9.2$ Hz), 6.93–7.02 (2H, m), 4.28–4.48 (8H, m), 3.79–3.92 (4H, m), 3.06–3.18 (6H, m), 2.64–2.84 (5H, m), 2.47–2.55 (3H, m), 2.34 (1H, m), 1.75–1.88 (3H, m), 1.55–1.63 (3H, m), 1.36–1.44 (2H, m), 1.25 (1H, m), 0.78–0.94 (3H, m).^{13}C-NMR (100 MHz, $CDCl_3$, δ) $\underline{174.27,\ 174.09}$, $\underline{173.33,\ 173.22}$, 166.68, 155.01, $\underline{153.01,\ 152.98}$, 142.18, $\underline{133.29,\ 133.27}$, 116.21 (two carbons), 112.73, 110.87, $\underline{97.58,\ 97.54}$, 61.60, 61.04, 60.84, $\underline{51.24,\ 51.18}$, $\underline{50.52,\ 50.49,\ 50.44}$, 49.28, $\underline{48.65,\ 48.56}$, 44.33, $\underline{41.97,\ 41.94}$, $\underline{41.22,}$

41.10, 40.51, 39.79, 39.66, 36.63, 36.61, 36.35, 29.73, 29.62, 27.91, 27.88, 26.98, 26.94, 23.92, 23.88. Underlined numbers are sets of ^{13}C peaks at the same position in the diastereomers or in substituents R and R'.

Spin-coated films of the chromophores dispersed in polymers were prepared as follows. In the spectral measurements depending on concentration of **1a** and **1b**, 5 mg of the mixture of the chromophore and PCZ-300 (poly(oxycarbonyloxy-1,4-phenylenecyclohexane-1,1-diyl-1,4-phenylene), Mitsubishi Gas Chemical) in a given weight concentration was dissolved in 0.5 mL of chloroform. In the poling experiments, **1a** (1 mg) and PCZ-300 (5 mg) were dissolved in 1 mL of chloroform. For **2c** and **2d**, 1 mg of the chromophore and 10 mg of PMMA (poly(methyl methacrylate), $M_w = 1.2 \times 10^5$, Aldrich) were dissolved in 1 mL of chloroform. Glass slides, on which the solution was dropped, were spun at 500 rpm for 10 s and then at 1000 rpm for 30 s. For the corona poling, the spin-coated film on the glass slide was put on a grounded copper plate, which was placed on a temperature-controllable heater. A positive voltage to the copper plate was applied from a tungsten needle setting 1 cm above the film.

3. Results and discussion

The μ and β values were calculated by using PM5 (MOPAC 2002 Ver. 2.5.0) for the structure optimized by using D-VWN DFT (DGauss Ver. 4.1). The μ and β of **1** with methyl groups as R and R' were obtained to be 12.6 D and 341×10^{-30} esu, respectively, while those of **2** with methyl groups as R and R' were 10.6 D and 127×10^{-30} esu, respectively. Namely, $\mu\beta$ of **1** is aproxymately 3.2 times as large as that of **2**. Thus, the effect on alkyl chain types was examined on **1** because the molecular length of **1** is longer than that of **2** and aggregation formation of **1** seemed to be easier than that of **2**.

When 10 wt% of **1b** with linear alkyl groups was dispersed in the polymer, absorption maximum wavelength (λ_{max}) was observed at 729 nm (Figure 2 (b)). However, in the 40 wt% sample, the blue-shifted sharp band appeared at 625 nm due to formation of the H-type aggregates. On the other hand, **1a** did not show such a prominent peak due to H-type aggregation although blue shift of the λ_{max} was observed, i.e., the λ_{max} at 739 nm of the 10 wt% sample gradually moved to 680 nm in the 40 wt% sample (Figure 2 (a)). Bulkiness of the branched alkyl groups seemed to suppress the aggregation property of the chromophore. In addition, since we used racemic 2-ethyl-1-iodohexane as a reagent, **1a** is a mixture of three pairs of enantiomers to reduce crystallinity. In fact, the melting point range of **1a** is broad approximately between 100 and 117 °C and this is considered to be another factor for less aggregation. When the films in Figure 2 (a) were heated at 150 °C for 30 min, disaggregation was promoted and chromophore orientation induced during the spin-coating process was randomized to some extent, resulting in absorption maximum shifts to longer wavelengths, i.e., the λ_{max} of the 10 wt% and 40 wt% samples were observed at 757 nm and 715 nm, respectively (Figure 2 (c)). The spin-coated films of the 40 wt% samples of **1a**, **1b** and **1a** after heating at 150 °C for 30 min were observed by AFM (Figure 3). When the samples of **1a** and **1b** were compared, the average surface roughnesses (R_as) were 0.63 nm and 0.93 nm, respectively, and the maximum hight differences (R_zs) were 5.76 nm and 8.88 nm, respectively. Smaller values for **1a** seemed to be related to better misibility of **1a** to the polymer. For

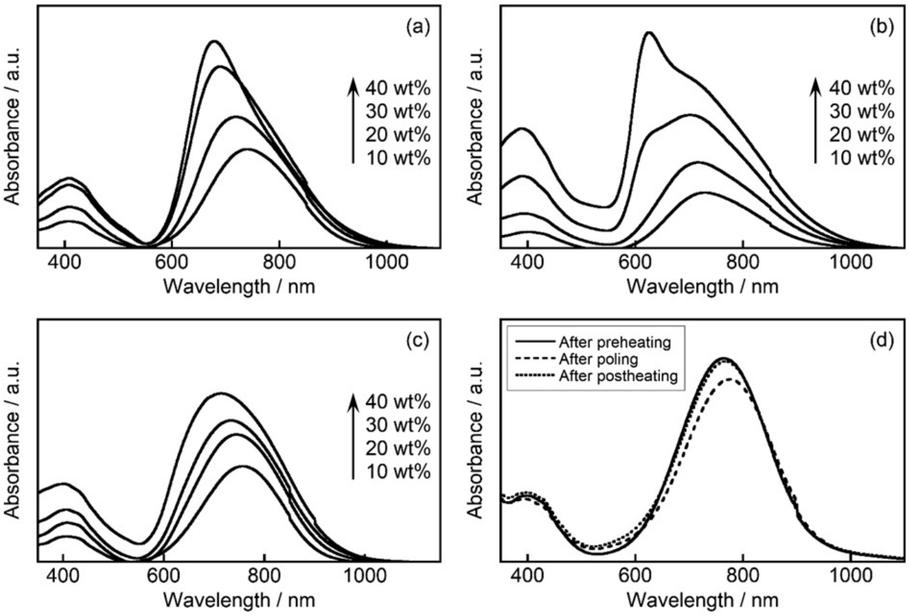

Figure 2. UV-visible-NIR absorption spectra of **1**: (a) Absorption changes depending on content of **1a** in PCZ-300; (b) absorption changes depending on content of **1b** in PCZ-300; (c) absorption of **1a** in PCZ-300 after heating at 150 °C for 30 min; (d) absorption changes of **1a** in PCZ-300 before and after corona poling. The preheated film was poled applying 4 kV at 140 °C for 5 min, and then postheated at 140 °C for 10 min to relax the orientation.

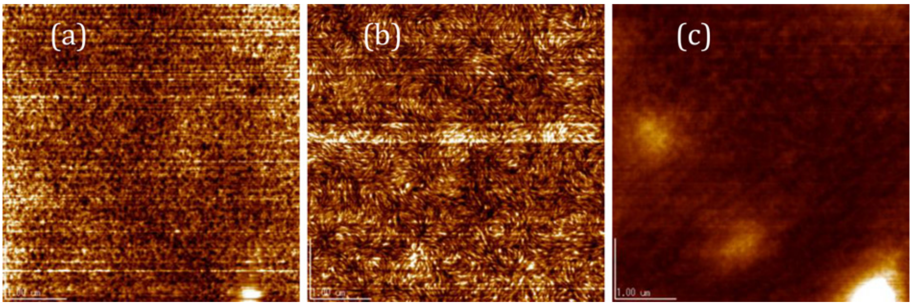

Figure 3. AFM topographic images of spin-coated films of **1**: (a) **1a** (40 wt%) in PCZ-300, (b) **1b** (40 wt%) in PCZ-300 and (c) **1a** (40 wt%) in PCZ-300 after heating at 150 °C for 30 min. The vertical and horizontal lines in the lower left corners in each image indicate 1 μm length.

the heated sample of **1a**, fine heterogeneous structures became ambiguous. On the other hand, large undulation, which was represented by the R_a of 1.74 nm and R_z of 25.8 nm, was observed although the mechanism for such thermal material transport is not clear. Corona poling was performed for the films of **1a** in PCZ-300, whose grass transition temperature was observed at approxymately 140 °C. For example, Figure 2 (d) shows absorption spectral changes of **1a** in PCZ-300 before and after corona poling applying 4 kV at 140 °C for 5 min. In this condition, the oriented chromophores were randamized after postheating at 140 °C for 10 min to recover the absorption to the preheating stage, indicating almost no damage of the chromophore. However, when the applied

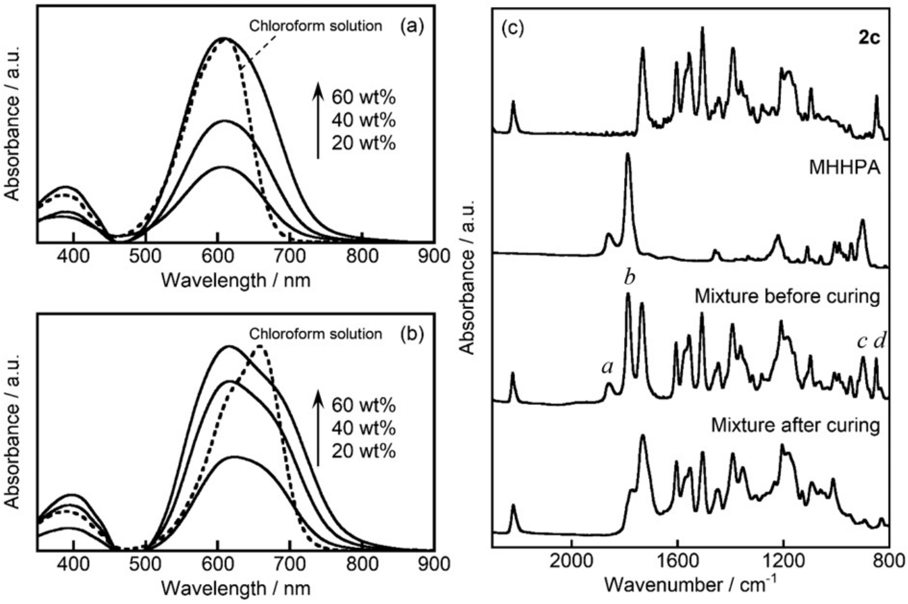

Figure 4. Absorption spectra of **2**: UV-visible absorption spectra of (a) **2c** and (b) **2d** in chloroform solution (dashed lines) and the absorption changes depending on content of the chromophores in PMMA; (c) IR absorption spectra of **2c**, MHHPA and the mixture of **2c**, MHHPA and DMBA (100:150:1) before and after curing.

voltage increased resulting in the poling current of more than 5 μA and/or the poling time increased, the chromophore degradation became prominent.

In addition to the aggregation problem, orientational relaxation of poled structures is another issue and crosslink of the chromophores is one of the solutions. In our previous studies, it was found that CDCOP chromophores were degraded especially by radical polymerization reactions stimulated by a photoinitiator [7], and thermal crosslinking process seemed to be better [8]. Epoxy group is a typical thermal crosslinkable moiety and it has been also applied to fix polar orientation of the nonlinear optical chromophores [12]. Thus, we synthesized **2c** with epoxide groups incorporated in the bulky norbornyl moiety to avoid aggregation of the chromophores. Due to the synthesis procedure of **2c**, the norbornyl substituents were confirmed to contain endo and exo stereoisomers, which were identified by the ^{13}C-NMR spectra [13]. Consequently, **2c** is a mixture of twenty pairs of enantiomers. This also affects lowering the crystallinity and the mixture has the broad melting point range approximately between 100 and 118 °C. Figure 4 (a) shows UV-visible absorption spectra of **2c** in chloroform and the absorption changes depending on content of **2c** in PMMA. The $\lambda_{\max}$ of the PMMA films was observed at 608 nm, which was not affected by the chromophore concentration. The $\lambda_{\max}$ of the chloroform solution was almost the same at 612 nm. On the other hand, the $\lambda_{\max}$ of **2d** with linear alkyl substituents showed a hypsochromic shift from 658 nm in chloroform to 616 nm in the 60 wt% PMMA film (Figure 4 (b)). This spetral difference is again considered to be originated from the aggregation property, i.e., **2d** is apt to form the aggregates compared with **2c**.

The crosslink reaction of **2c** was first examined by using boron trifluoride diethyl etherate as a Lewis acid. However, cleavage of ester groups preferentially occurred, and production of the corresponding alcohol derivative of **2c** and derivatives of 3-oxatricyclo[3.2.1.$0^{2,4}$]octane-6-carboxylic acid including 2-hydroxy-4-oxatricyclo[4.2.1.$0^{3,7}$]-nonan-5-one were confirmed by the NMR spectra. Thus, the crosslinking was performed in a basic condition using 4-methylhexahydrophthalic anhydride (MHHPA) as a hardener and *N*,*N*-dimethylbenzylamine (DMBA) as an accelerator. Chromophore **2c**, MHHPA and DMBA were mixed in 100:150:1 molar ratio and the mixture was cured first at 120 °C for 2 h and then at 150 °C for 48 h. The IR spectra of the mixture before and after curing are shown in Figure 4 (c) together with those of **2c** and MHHPA for comparison. In the spectrum of the mixture before curing, the peaks *a* at 1859 cm^{-1} and *b* at 1788 cm^{-1} can be assigned to symmetric and asymmetric C = O stretching of MHHPA, respectively. The peak *c* at 901 cm^{-1} is for C-O stretching of the acid anhydride framework of MHHPA. The peak *d* at 850 cm^{-1} is assignable to asymmetric ring deformation of the epoxide groups of **2c**. After curing, these peaks were apparently weakened indicating that the crosslink reaction between the epoxide groups of **2c** and MHHPA progressed. It was also confirmed by the fact that no chloroform-soluble portion was detected from the cured mixture. Since other characteristic IR peaks remained even after curing, the above crosslinking process seemed to be appropriated for orientation fixing of this chromophore.

4. Conclusion

In this study, the substituents of the CDCOP chromophores were modified to suppress the aggregation. For the thiophene-inserted CDCOP chromophores, introduction of 2-ethylhexyl groups was effective to avoid aggregation compared with the case of linear-alkyl substitution especially in the films with high chromophore content. In the experiments on orientation of the chromophore by corona poling and its relaxation by post-heating, clear decrease of absorbance and its almost quantitative recovery was observed, and there was no inconvenience due to bulkyness of the branched alkyl groups and serious damages of the chromophore. For the CDCOP chromophores directly bonded to the aniline moiety, norbornyl epoxide groups were introduced to satisfy both bulkiness to suppress aggregation and crosslink reactivity. The epoxide groups were confirmed to crosslink thermally with MHHPA in the presence of DMBA without serious damages of the chromophore. Effective poling process during crosslinking is in progress, and the thiophene-inserted CDCOP chromophore with norbornyl epoxide groups will be examined in the future study.

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