# Nonlinear Optical Side-Chain Polymers Post-Functionalized with High- $\beta$ Chromophores Exhibiting Large Electro-Optic Property

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**ABSTRACT:** Electro-optic side-chain polymers have been synthesized by the post-functionalization of methacrylate isocyanate polymers with novel phenyl vinylene thiophene vinylene bridge (FTC) nonlinear optical chromophores. For this application, FTC-based chromophores were modified in their electronic donor structure, exhibiting much larger molecular hyperpolarizabilities compared with the benchmark FTC. Of these new chromophores, absorption spectra, hyper-Rayleigh scattering experiment, and thermal analysis were carried out to confirm availability as effective nonlinear optical units for electro-optic side-chain polymers. The electro-optic coefficients ( $r_{33}$ ) of obtained polymers were investigated in the process of *in situ* poling by monitoring the temperature, current flow, poling field, and electro-optic signal. Compared with the non-

**INTRODUCTION** During the past several decades, there has been growing interest in organic and polymeric electro-optic (EO) materials due to their potential applications in telecommunication, digital signal processing, THz generators, and photonic nano-micro devices.<sup>1-5</sup> This trend of increasing interest continues in the development of a significantly high EO coefficient ( $r_{33}$ ); higher than 100 pm/V at telecommunication wavelengths. Such high EO performance has allowed for Mach-Zehnder modulators with low driving voltage of <1 V, which makes this class of devices very attractive for high-bandwidth operation. These devices have shown optical modulations up to 100 GHz in commercial devices and up to 1.6 THz experimentally.<sup>6–9</sup> Such performance has demonstrated EO activity 10 times that of the inorganic counterparts (LiNbO<sub>3</sub>:  $r_{33} \sim 32$  pm/V).

For promising applications of novel nonlinear optical (NLO) chromophores, which play the key role in EO devices, a strong need remains for improving the optical properties and thermal stability, both at the molecular level and as processed materials, to fulfill requirements for device fabrication processes and long-term operation. For these material

substituted analogue, benxyloxy modified FTC chromophore significantly achieved higher nonlinear optical property, exhibiting molecular hyperpolarizability at 1.9  $\mu$ m of 4600  $\times$  10<sup>-30</sup> esu and an  $r_{33}$  value of 150 pm/V at the wavelength of 1.31  $\mu$ m. Synthesized electro-optic polymers showed high glass transition temperature ( $T_g$ ), so that the temporal stability examination exhibited >78% of the electro-optic intensity remaining at 85 °C over 500 h. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 47–54, 2011

**KEYWORDS:** electro-optic coefficient; electro-optic polymer; functionalization of polymer; molecular hyperpolarizability; NLO; poling; side-chain polymer; thermal properties

characteristics to be realized, molecules with large molecular hyperpolarizability ( $\beta$ ), high decomposition temperatures, and high solubility in polymer hosts are eagerly anticipated. For increasing  $\beta$  values, a series of NLO chromophores via the invention of extended polyene-bridges or conjugated thiophene-bridge systems with strong tricyano-containing heterocyclic electron acceptors has been reported.<sup>10-16</sup> In Figure 1, examples of these designs are highlighted by what are known as phenyltetraene bridge (denoted CLD-type) and phenyl vinylene thiophene vinylene bridge (denoted FTCtype) chromophores. We recently achieved a significant improvement of molecular hyperpolarizability and EO property for FTC-based chromophores (A-C), as shown in Figure 1. These chromophores have an additional electron-donating effect on the conjugated bridge despite being highly comparable to their 4-dialkylaminoaryl analogs. The enhancement of both microscopic  $\beta$  values and macroscopic  $r_{33}$  values is significant for these chromophores over FTC and CLD benchmarks. By using chromophore **B** or **C** for example, the EO measurement in PMMA host after electric poling gained experimental  $r_{33}$  over 100 pm/V, presenting about two-fold improvement over FTC benchmarks. Though obtained EO

Additional Supporting Information may be found in the online version of this article. Correspondence to: S. Yokoyama (E-mail: s\_yokoyama@cm. kyushu-u.ac.jp)

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FIGURE 1 Structures of NLO chromophores CLD, FTC, and donor-modified chromophores (A–C) with additional methyloxy, benzyloxy, and TBDMS groups.

property has the higher level reported so far in the series of FTC-based chromophores, further increment is limited by the chromophore dipolar interaction and aggregation in the polymer host at higher concentrations.

Toward the high EO polymer preparation and high temperature resistance, the covalent attachment of side-chain NLO chromophores onto polymer backbones offers many advantages over the host-guest materials. However, synthesis of side-chain polymers often caused degradation of the fragile chromophores during the polymerization process. Post-functionalization of an already prepared precursor polymer by NLO chromophores is a simple, alternative synthetic approach to classical polymerization or complicated chromophore-polymer composites.<sup>17–19</sup> First, the starting polymer was prepared separately without exposing the NLO chromophore to harsh polymerization condition. Then, NLO chromophores were attached to the polymer backbone under a mild reaction condition in high yields with a minimum release of by-products. This strategy therefore allows optimization of a given property, such as EO coefficients or thermal stability, through the large variety of different materials and synthetic conditions.

In this article, we report details of the synthesis and optical properties of a class of EO side-chain polymers post-functionalized with high- $\beta$  chromophores. Our primary efforts have been focused on developing EO polymers with efficient electronic structure for both increasing nonlinear optical properties and stabilizing at a higher temperature. A poly[(methyl methacrylate)-*co*-(2-methacryloyloxyethyl isocyanate)] (PMMA-*co*-MOI) is selected as polymeric backbone for the post-functionalization system because of the simple attachment of NLO chromophores and the expected high temperature property through urethane-bond formation.<sup>20</sup> Therefore, high- $\beta$  chromophores **A** and **B** shown in Figure 1 are mono-hydroxyalkyl

functionalized and tethered on PMMA-*co*-MOI backbone as the NLO units. The nonsubstituted FTC benchmark is also, likewise, functionalized and processed for comparison.

#### **EXPERIMENTAL**

# **Materials and Instruments**

All the reagents and solvents were purchased from commercial sources and used as received. 2-Methacryloyloxyethyl isocyanate was from Showa Denko (Japan). Column chromatography was performed using silica gel (Kanto Chemical, 60N).<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JNM-LA400 spectrometer with tetramethyl silane as a reference. High-resolution mass spectrometry (ERMS) was performed by JEOL MStation JMS 700. Thermo gravimetry-differential thermal analysis (TG-DTA) was performed using a SII-TG/ DTA 6200 in nitrogen atmosphere at a heating rate of 5 °C/ min. Differential scanning calorimetry (DSC) was performed using a SII-DSC 6220 in nitrogen atmosphere at a heating rate of 5 °C/min. The molecular weight and polydispersity of the polymer were determined by size exclusion chromatography using a Shodex GPC K-804L column on a JASCO LC2000 liquid chromatography system with THF as an eluent and with a polystyrene standard calibration. UV-visible spectra were recorded with a Shimadzu UV-vis spectrometer 1240. FT-IR spectra were recorded with a Shimadzu FT-IR spectrometer 8400S.

#### Synthesis

The mono-hydroxyalkyl donor units, chromophores, and side-chain polymers were synthesized as shown in Schemes 1–3. The detailed synthetic procedures are as follows. <sup>1</sup>H and <sup>13</sup>C NMR spectra data and thermal properties of polymers were submitted in Supporting Information.





SCHEME 2 Synthesis of mono-hydroxylated chromophores.

# 3-Methoxy-N-methylaniline (2a)

To a suspension of NaOMe (15.8 g, 292 mmol) in MeOH (70 mL) was added *m*-anisidine **1a** (6.0 g, 48.8 mmol). The resulting solution was poured into a suspension of paraformaldehyde (2.22 g, 73.9 mmol) in MeOH (25 mL). After stirring at room temperature for 24 h, NaBH<sub>4</sub> (1.85 g, 48.9 mmol) was added to the mixture. After reflux for 2 h, the mixture was evaporated to 1/2 volume, treated with 1 M KOH (200 mL), and then extracted with dichloromethane. The organic extracts were dried over MgSO<sub>4</sub> and evaporated to afford **2a** (5.71 g, 86.4%).

#### Ethyl 2-[(3-Methoxyphenyl)-N-methylamino]acetate (3a)

A solution of **2a** (7.71 g, 41.7 mmol) and ethyl bromoacetate (8.36 g, 50 mmol) in acetonitrile (50 mL) together with NaHCO<sub>3</sub> (3.85 g, 45.8 mmol) was stirred and refluxed under nitrogen for 4 h. At room temperature triethylamine (2 mL) was added and then filtrated and evaporated. The residue was dissolved in dichloromethane, washed with water, dried,

and evaporated. The ester **3a** was obtained as a clear liquid (8.24 g, 88.6%).

#### 2-[(3-Methoxyphenyl)-N-methylamino]ethanol (4a)

A suspension of sodium borohydride (2.79 g, 73.8 mmol) and lithium bromide (6.41 g, 73.8 mmol) in dry THF (80 mL) was reflux under nitrogen for 1 h. A solution of the ester **3a** (8.24 g, 26.9 mmol) in THF (10 mL) was added at room temperature and the mixture was refluxed for a further 5 h. The solvent was evaporated and the residue was treated slowly with 1 M KH<sub>2</sub>PO<sub>4</sub> (200 mL) and stirred until hydrogen evolution ceased, and then extracted with dichloromethane. The organic extracts were washed with saturated aqueous NaHCO<sub>3</sub>, dried, and evaporated. The hydroxylated donor **4a** was obtained as a clear liquid (10.12 g, 72.4%).

# Pivalic Acid 2-[(3-Methoxyphenyl)-*N*-methylamino]ethyl Ester (5a)

Pivaloyl chloride (7.38 g, 61.2 mmol) was added dropwise under nitrogen to a mixture of 4a (5.54 g, 30.6 mmol) and



**SCHEME 3** Synthesis of PMMA-MOI and side-chain polymers.

pyridine (7.26 g, 91.8 mmol) in toluene (100 mL). The reaction mixture was stirred at room temperature for 1 h, and then heated at 85 °C for further 3 h. After cooling at room temperature, the resulting salt was separated, and the solvent was evaporated. The residue was dissolved in ethyl acetate, washed with water, dried, and evaporated. The crude product was purified by silica chromatography (ethyl acetate: hexane = 1:3) to give color less oil **5a** (7.58 g, 93.2%).

# Pivalic Acid 2-[(4-Formyl-3-methoxyphenyl)-Nmethylamino]ethyl Ester (6a)

To a solution of POCl<sub>3</sub> (2.89 g, 18.8 mmol) in DMF (15 mL) was added 5a (5.0 g, 18.8 mmol) in DMF (5 mL) under nitrogen at 0  $^\circ\text{C}.$  After stirring for 16 h at room temperature, the mixture was treated with 20% sodium acetate solution (50 mL), and then extracted with ethyl acetate. The organic extracts were washed with saturated aqueous NaHCO<sub>3</sub>, dried, and evaporated. The crude product was purified by silica chromatography (ethyl acetate:hexane = 1:2) to give pale yellow oil 6a (5.0 g, 90.6%).

# Pivalic Acid 2-{[3-Methoxy-4-(2-thiophen-2-ylvinyl)phenyl]-*N*-methylamino}ethyl Ester (8a)

To a solution of PhLi (1.64 g, 19.6 mmol, 19% in Bu<sub>2</sub>O solution) in THF (50 mL) at 0 °C was added 2-thenyl triphenylphosphonium chloride 7 (6.4 g, 16.3 mmol) under nitrogen. The solution was maintained at this temperature during the dropwise addition of a solution of 6a (4.0 g, 13.6 mmol) in THF (15 mL). After stirring 1.5 h, the reaction mixture was poured into water. The organic phase was extracted by ethyl acetate, washed with brine, dried, and evaporated. The crude product was purified by silica chromatography (ethyl acetate:hexane = 1:4) to give **8a** (E/Z mixture) as a yellow oil (4.03 g, 97.3%).

# 2-(tert-Butyldimethylsiloxyethyl)[3-methoxy-4-(2-thiophen-2-yl-vinyl)phenyl]-N-methyl-amine (9a)

To a solution of NaOH (4.28 g, 107 mmol) in EtOH (25 mL) and water (7 mL) was added 8a (4.0 g, 10.7 mmol) in EtOH (10 mL). The solution was warmed at 40 °C and stirred for 1 h, then diluted with water and extracted with ethyl acetate. The organic extracts were washed with water, dried, and evaporated. The resulting yellow oil was solved in DMF (8 mL) with imidazole (1.47 g, 21.6 mL). To this mixture, tert-butyldimethylsilyl chloride (2.4 g, 16.2 mmol) in DMF (5 mL) was added dropwise at room temperature, and stirred for 1.5 h. The mixture dissolved in ethyl acetate, washed with water, dried, and evaporated. The crude product was purified by silica chromatography (ethyl acetate:hexane = 1:3) to give **9a** (*E*/*Z* mixture) as a yellow oil (4.30 g, 98.6%).

# 5-[2-(4-{[2-(tert-Butyldimethylsiloxyethyl)]-Nmethylamino}-2-methoxyphenyl)-vinyl]thiophene-2-carbaldehyde (10a)

A solution of 9a (4.30 g, 10.7 mmol) in THF (30 mL) was cooled to -78 °C and maintained at this temperature during the dropwise addition of n-BuLi in hexane (1.6 M, 10 mL, 15.7 mmol). Following 1 h of stirring at -78 °C the temperature was maintained prior to the dropwise addition of DMF (0.95 g, 12.3 mmol). After 1 h, solution was gradually

warmed to 0 °C before being quenched (H<sub>2</sub>O, 10 mL). The reaction mixture was poured into water, extracted by dichloromethane, washed with brine, dried, and evaporated to give a crude oil. The oil was solved in toluene with iodide (0.20 g). The solution was allowed to stir at room temperature for 30 min. Then, the mixture was washed with aqueous NaHSO<sub>3</sub> (5%) and brine, dried, and evaporated. The crude product was purified by silica chromatography (ethyl acetate:hexane = 1:3) to give **10a** (*E* form) as an orange-red solid (4.04 g, 87.4%).

# 5-(2-{4-[(2-Hydroxyethyl)-N-methylamino]-2-methoxyphenyl}vinyl)thiophene-2-carbaldehyde (11a)

To a solution of 10a (4.04 g, 9.4 mmol) in THF (200 mL) at room temperature was added dropwise the solution of NBu<sub>4</sub>NF<sub>4</sub> in THF (1 M, 2.5 mL, 2.5 mmol). The mixture was stirred at room temperature for 1 h. After removal of the solvent, crude product was purified by silica chromatography (ethyl acetate:hexane = 2:1) to give **11a** (*E* form) as an orange-red solid (2.25 g, 75.5%).

# **Chromophore (13a)**

To a solution of 11a (1.02 g, 2.59 mmol) in THF (8 mL) and EtOH (25 mL) was added the acceptor 12 (0.82 g, 2.59 mmol). The reaction was allowed to stir at room temperature for 48 h. The product was collected by filtration, washed with cold EtOH (20 mL, 5 times). Chromophore 13a (E form) was purified by silica chromatography (dichloromethane:methanol = 10:0.5) to give a dark brown solid (1.42 g, 79.3%). HRMS (ESI) (M<sup>+</sup>, C<sub>33</sub>H<sub>25</sub>O<sub>3</sub>N<sub>4</sub>F<sub>3</sub>S): calcd, 614.1599; found, 614.1595 [M<sup>+</sup>].

# Chromophore (13b)

In a similar manner, as shown in Schemes 1 and 2, 13b was synthesized from **1b**. HRMS (ESI)  $(M^+, C_{39}H_{29}O_3N_4F_3S)$ : calcd, 690.1912; found, 690.1908 [M<sup>+</sup>].

# Chromophore (13c)

In a similar manner, as shown in Scheme 2, 13c was synthesized from 2-(N-methylanilino)ethanol (4c) as the benchmark. HRMS (ESI) (M<sup>+</sup>, C<sub>33</sub>H<sub>25</sub>O<sub>2</sub>N<sub>4</sub>F<sub>3</sub>S): calcd, 598.1650; found, 598.1655 [M<sup>+</sup>].

## Precursor Polymer (PMMA-co-MOI)

Methyl methacrylate (MMA, 2.0 g, 20.0 mmol), 2-methacryloyloxyethyl isocyanate (MOI, 0.78 g, 5.0 mmol), and azobisisobutyronitrile (AIBN, 0.08 g, 0.49 mmol) were dissolved in toluene (10 mL) under nitrogen. The mixture was stirred at 65 °C for 3 h to yield a viscous solution. The resulting product was poured into hexane to induce precipitation. The polymer was collected by filtration, washed with hexane several times, and dried at 40 °C in vacuo. The yield was 2.27 g (81.6%) of a white solid.

# **General Procedure for Preparation of Side-Chain Polymer**

PMMA-co-MOI (0.5 g, 1 equiv) and chromophore 13a (0.33 g, 40 wt % equiv) were dissolved in THF (25 mL) under nitrogen at room temperature. A trace amount of dibutyltin dilaurate (DBTDL) was added, and the mixture was stirred for 24 h. To complete the reaction, MeOH (2 mL) was added to the mixture, and stirred for a further 12 h. The reaction mixture was poured into methanol, and the precipitated polymer was filtrated. To purify the NLO side-chain polymer, precipitation was repeated several times for the removal of unreacted chromophore. The product was dried to yield 0.78 g of a dark green solid. In a similar manner, polymers were post-functionalized by the chromophore at different concentrations between 30 and 50 wt % equiv. Chromophores **13b** and **13c** (benchmark) were also used to synthesize the side-chain polymers.

#### **RESULTS AND DISCUSSION**

#### **Chromophore and Polymer Syntheses**

The synthesis of mono-hydroxyalkyl chromophores (13a-c) is shown in Schemes 1 and 2. The synthesis of starting donor 4a began from N-methyl-m-anisidine 2a, the preparation of which was approached from *m*-anisidine **1a** by treatment with NaOMe and formaldehyde in methanol, followed by reduction with NaBH<sub>4</sub>. Compound 2a was alkylated by ethyl bromoacetate to give ester 3a, which was smoothly reduced to alcohol 4a with NaBH<sub>4</sub>-LiBr in THF. The reaction of compound 4a with pivaloyl chloride was effected to protect the hydroxyl group on the donor of the chromophore. Subsequent reaction with DMF and POCl<sub>3</sub> afforded 4-amino-2-methoxybenzaldehyd 6a. Thiophene bridge compound 7 was prepared in two steps to yield the Witting salts. After the Witting condensation of 7 with aldehyde 6a, desired donor bridge 8a was produced in high yield. The pivaloyl protecting group on the donor end was replaced with TBDMS group to afford compound 9a that was then formylated effectively with n-BuLi and DMF to give 10a. The TBDMS protecting group was cleaved under the acidic condition to yield mono-hydroxyalkyl donor bridge 11a. The acceptor 12 was coupled to the conjugation bridge by Knoevenagel condensation to afford mono-hydroxyalkyl chromophore 13a. Chromophores 13b and 13c were also synthesized through the similar process by using starting compound 1b and 2-(N-methylanilino)ethanol (4c), respectively. TG-DTA measurement indicated that synthesized chromophores had high temperature resistance: their decomposition temperatures ( $T_d$ ) are around 210 °C as summarized in Table 1.

The side-chain polymers were synthesized by utilizing a copolymer, poly[(methyl methacrylate)-*co*-(2-methacryloyloxy-

**TABLE 1** Physical and Optical Properties ofMono-Hydroxy Chromophores

Chromophores	λ <sub>max</sub> ª (nm)	$eta^{ ext{b}}$ ( $ imes$ 10 $^{-30}$ esu)	<i>Т</i> <sub>d</sub> (°С)
13a	766	4400	215
13b	768	4600	210
<b>13c</b> (benchmark)	734	2800	207

<sup>a</sup>  $\lambda_{max}$  are measured in chloroform.

<sup>b</sup>  $\beta$  values are measured in chloroform using the HRS technique at the laser wavelength of 1.9  $\mu$ m. $T_{\rm d}$  is the onset decomposition temperature measured by TGA under nitrogen at a heating rate of 5 °C/min.



FIGURE 2 Absorption spectra of synthesized chromophores 13a, 13b, and 13c (benchmark) in chloroform.

ethyl isocyanate)] (PMMA-co-MOI), with around 20 mol % of the isocyanate moieties. PMMA-co-MOI was prepared by free-radical polymerization in toluene at 65 °C using AIBN as the initiator. After the polymerization, mono-hydroxyalkyl chromophores were attached to the precursor polymers with different concentrations between 20 and 50 wt % through a simple urethane-forming reaction. By using DBTDL as a catalyst, these post-functionalization reactions proceeded smoothly in THF at room temperature. The reaction was monitored using FT-IR spectroscopy. At 2272 cm<sup>-1</sup>, isocyanate stretching vibration was observed to decrease significantly during the reaction. To block an excess of unreacted isocyanete after post-functionalization, MeOH was added to complete the residual reaction. Completion of the reaction was determined by the disappearance of the isocyanate stretching vibration in the FT-IR spectrum.

# Absorption Spectroscopy and Molecular Hyperpolarizability of NLO Chromophores

Linear and nonlinear optical properties of synthesized chromophores are summarized in Table 1. All of mono-hydroxyalkyl chromophores **13a-13c** were well dissolved in chloroform and the absorption spectra were recorded to determine the maximum absorption ( $\lambda_{max}$ ) of the  $\pi$ - $\pi^*$  charge-transfer band. The benchmark **13c** showed  $\lambda_{max}$  at 734 nm in a CHCl<sub>3</sub> solution as shown in Figure 2. The addition of methyloxy and benzyloxy groups on the donor unit led to a shifting of the charge-transfer absorption to the lower energy region:  $\lambda_{max}$  to 766 and 768 nm for **13a** and **13b**, respectively, implying an extra electron-donating strength to the  $\pi$ -conjugated bridges.

The molecular hyperpolarizability ( $\beta$ ) of chromophores was measured in chloroform using hyper-Rayleigh scattering (HRS) measurement at the wavelength of 1.9  $\mu$ m.<sup>21,22</sup> The result of  $\beta$  values is summarized in Table 1. The technique allows the direct evaluation of  $\beta$ , employing the reference chromophore with known  $\beta$  value. In this study, FTC was

**TABLE 2** Physical Properties of Side-Chain Polymers

Polymers	<i>M</i> <sub>w</sub> (×10 <sup>4</sup> )	$M_{\rm w}/M_{\rm n}$	Chromophore (wt %)	<i>T</i> g (°C)	<i>T</i> d (°C)
14a	4.15	2.3	35	138	295
14b	3.68	2.3	36	135	296
14c	2.85	2.2	34	147	282

used as the external standard.<sup>23</sup> HRS analysis indicated that the addition of donor group is effective in increasing the  $\beta$ values. The factor of increase in the  $\beta$  of **13a** and **13b** were 1.57 and 1.64 by comparison with benchmark **13c**. The result of  $\beta$  enhancement by the addition of methoxy and benzyloxy groups was consistent with the  $\lambda_{max}$  shift of these chromophores to the longer wavelengths.

#### **Characterization of Side-Chain Polymers**

Physicochemical properties of synthesized side-chain polymers are summarized in Table 2. The loading concentration of chromophores in the side-chain polymers (14a-14c) were determined by measuring the absorption spectra, which were compared with the bare chromophores (13a-13c) with known concentration. The obtained side-chain polymers are highly soluble in a common organic solvent such as chloroform, THF, cyclopentanone, or DMF. The size exclusion chromatography analysis indicated the weight average molecular weight  $(M_w)$  of polymers in the range of 28,500-41,500. DSC analysis showed that the glass transition temperatures  $(T_{\sigma})$  of the side-chain polymers increased as the loading concentration of chromophores. At 34-36 wt %  $T_{\rm g}$ values of 14a, 14b, and 14c were 138, 135, 147 °C, depending on the structure of the chromophores. TG-DTA showed no decomposition below 280 °C. These  $T_{\rm g}$  and  $T_{\rm d}$  data were used to determine the suitable poling temperature and decomposition point for the process of EO measurements.

#### **EO Properties of Side-Chain Polymers**

According to the enhanced molecular hyperpolarizabilities for chromophores 13a and 13b compared with benchmark 13c, an improvement of macroscopic EO property for the sidechain polymers is expected by post-functionalization reaction. Side-chain polymers 14a-14c dissolved in cyclopentanone (filtrated through a 0.2  $\mu$ m syringe filter) were spin-coated onto indium tin oxide (ITO) glass substrate to produce films of about 2  $\mu$ m thickness. After baking in a vacuum oven overnight at 85 °C to remove the residual solvent, a thin gold layer with a thickness of 100 nm was sputtered on the films as the top electrode for electric poling. The *in situ*  $r_{33}$  measurement at the laser wavelength of 1.31  $\mu$ m was performed by a modified Teng-Mann reflection method.<sup>24,25</sup> In this measurement,  $r_{33}$  signals were collected during the process of heating and cooling in the presence of a poling field. The  $r_{33}$  value was directly obtainable according to the equation:

$$r_{33} = \frac{3\lambda}{4\pi n^2} \frac{I_{\rm m}}{V_{\rm m}I_{\rm c}} \frac{(n^2 - \sin^2\theta)^{\frac{1}{2}}}{\sin^2\theta} \sim \frac{I_{\rm m}}{I_{\rm c}}$$
(1)

where  $\theta$ , *n*, and  $V_{\rm m}$  are the incident angle of laser, refractive index at  $\lambda = 1.31~\mu{\rm m}$ , and AC electric modulation field,

respectively.  $I_{\rm m}$  is the measured modulated-light intensity having the same frequency as the AC modulation field, and  $I_{\rm c}$ is the unmodulated-light intensity when phase retardation is 90° between the TE and TM mode. The intensity change was detected using a lock-in amplifier isolating the moderated signal,  $I_{\rm m}$ . Overlaying a DC poling field ( $V_{\rm p}$ ) with  $V_{\rm m}$ , realtime monitoring of the ratio  $I_{\rm m}/I_{\rm c}$  allowed direct evaluation of optimum  $r_{33}$  values under the controlled experimental parameters such as current, temperature, and applied voltage.

A representative in situ poling process using side-chain polymer 14b is shown in Figure 3(a-d). The loading concentration of the chromophore is 36 wt %. In a general experiment, the sample was mounted on the poling stage and the temperature was increased in several minutes up to around  $T_{g}$ . The poling field was then applied to the sample at a ramping rate of 8 V/min. During the poling process, the electric current was monitored to optimize poling efficiency and to control local electrical breakdown in the films. As shown in Figure 3(c), the current grew rapidly with the ramping of poling field, and maximized at 480  $\mu$ A when the poling field climbed to 60 V/ $\mu$ m. The increment of current should be dominantly ascribed to the chromophore alignment under the external electric field and the rearrangement of polymer, which is mostly accomplished around the  $T_{\rm g}$  of polymer. The monitoring of the current also enabled more efficient poling of the sample. Generally, the breakdown of the electric field through the polymeric film is accompanied by an abrupt overflow of the electric current. Thus, the ramping of the poling field ceased and maintained at 86 V/ $\mu$ m when the second increasing trend of the current flow appeared in



**FIGURE 3** *In situ* plots of poling process on a representative sample of side-chain polymer **14b** containing 35 wt % of NLO chromophore. (a) Temperature, (b) flowing current, (c) applied field, and (d)  $r_{33}$ , are plotted during the poling process.

Figure 3(c). The current dropped slowly after peaking, and even the poling field maintained a constant value. This may be due to the changing complexity of charge injection and trapping behavior of polymer with high chromophore concentration. Figure 3(d) indicates that the  $r_{33}$  varied simultaneously with the applied voltage and reached its maximum of 193 pm/V at the poling field of 86 V/ $\mu$ m. Such a value leveled off under the continuous poling field at 138 °C, resulting in *in situ* poling efficiency of 2.3 (nm/V)<sup>2</sup> defined as the ratio of  $r_{33}$  and  $V_{\rm p}$ . The sample was then cooled to room temperature with the poling field maintained. During the rapid cooling process, there was a notable relaxation phenomenon of the molecular ordering as the total EO signal decreased by 24%. At the same time, the current also declined from 300 to 20  $\mu$ A due to the remarkable increase of resistivity of the polymeric sample. Eventually,  $r_{33}$  of 150 pm/V was realized at room temperature for the poled electro-optic film after removing the poling field. Poling efficiency of 1.7  $(nm/V)^2$  was estimated for the polymer 14b. Measured electro-optic property is much higher than the reported  $r_{33}$  values (50-70 pm/V) for host-guest NLO polymers using standard FTC analogues in PMMA.<sup>16</sup>

To investigate the optimum chromophore concentration for the EO property, series of side-chain polymers was synthesized with the different chromophore concentrations in the range of 22–46 wt %. Each sample was poled around its  $T_g$ by *in situ*  $r_{33}$  monitoring method for optimal experiments. As shown in Figure 4,  $r_{33}$  values of three groups increased with rising chromophore contents at lower concentration range. This observation is consistent with the fact that the EO coefficient is directly proportional to the chromophore number density. The resultant  $r_{33}$  obtained under the optimal poling conditions are summarized in Table 3. The highest  $r_{33}$  values of the films **14a**, **14b**, and **14c** were obtained with the chromophore concentrations of 35, 36, and 34 wt %, respectively. The highest  $r_{33}$  value of 150 pm/V was achieved for



FIGURE 4 Dependence of EO property of side-chain polymers 14a, 14b, and 14c with the different chromophore concentrations.

Polymers <sup>a</sup>	r <sub>33</sub> <sup>b</sup> (pm/V)	r <sub>33</sub> /V <sub>p</sub> (nm/V) <sup>2</sup>	Temporal Stability <sup>c</sup> (%)
14a	97	1.2–1.4	72
14b	150	1.6–1.8	78
14c	75	1.0–1.2	68

<sup>a</sup> Polymers contain chromophores at 35, 36, and 34 wt % for **14a**, **14b**, and **14c**, respectively.

<sup>b</sup> EO coefficient measured at 1.31  $\mu$ m.

 $^{\rm c}$  EO property measured after 500 h at 85  $^{\circ}\text{C}.$ 

side-chain polymer 14b containing 36 wt % of chromophore. The result fully reflects the varying trend of  $\beta$  of chromophores: 13b > 13a > 13c. Though chromophore 13b has about 5% higher  $\beta$  value than that of **13a**, benzyloxy substituent at the donor part should be intended to prevent the strong electrostatic interaction between chromophores. This implies that the additional donor group on the donor part of the chromophore had a much profound effect on the electric-induced chromophore alignment, where polymer 14b showed 50% larger poling efficiency than that for 14a and **14c**. After reaching the maximum  $r_{33}$  value at the optimum chromophore density, EO property tended to decrease at higher loading range (>42 wt %). This is undoubtedly attributed to the strong dipole-dipole interaction, which leads to chromophore anti-parallel orientation that partially cancels the acentric symmetry.

According to the thermal analyses by DSC and TGA, sidechain polymers showed high  $T_{\rm g}$  ranging from 135 °C to 147 °C and  $T_{\rm d}$  higher than 280 °C. Though high  $T_{\rm g}$  of the EO polymer is favorable for maintaining chromophore alignment stability, a certain reduction of EO property is inevitably accompanied in the long-term application. Long-term alignment stability was recorded by heating the poled samples at 85 °C and measuring the  $r_{33}$  values at various point of



FIGURE 5 Temporal stability of side-chain polymers 14a, 14b, and 14c containing about 35 wt % of NLO chromophores at 85 °C for 500 h.

extended time as shown in Figure 5. For all of samples, electro-optic property showed an initial fast decay during the first 20 h, whereas 68–78% of  $r_{33}$  value could be maintained at 85 °C for over 500 h. This owes to, first, the advantage of the side-chain polymer strategy, by which the NLO chromophore is post-functionalized on the polymer backbone through a thermally stable urethane bond. Second, the large volume of the benzyloxy group attached on the chromophore favors retarding the relaxation of its alignment and to "freezing" the aligned order.

#### CONCLUSIONS

In conclusion, we have synthesized three groups of electrooptic side-chain polymers by using the convenient urethaneforming post-functionalization of mono-hydroxyl chromophores on PMMA-co-MOI backbone. We used FTC-based chromophore as NLO unit, where the modification on the donor units by attaching an additional functional group led to a significant improvement of both microscopic hyperpolarizability ( $\beta$ ) and macroscopic electro-optic coefficient ( $r_{33}$ ). As a result, the side-chain polymer was poled up to 150 pm/V and exhibited about two-fold improvement over the counterpart polymer. The enhanced donor also contributed to maintain temporal stability of the poled side-chain polymer through retardance of flexibility of aligned chromophores. Up to 78% of the intensity ultimately remained after annealing at 85 °C for over 500 h. Therefore, the electro-optic side-chain polymer not only successfully increased the  $r_{33}$  values by delaying the occurrence of intermolecular interaction on the chromophore concentration scale, but also considerably enhanced the thermal stability for the real device applications.

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