Development of Organic Electro-Optic Materials and its Evaluation Techniques

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The resent development of organic electro-optic materials and its evaluation techniques are described in the present paper. The molecular design of electro-optic (EO) chromophores to improve the value of hyperpolarizablity (β), which is one of the important parameters to increase the electro-optic coefficient, is described. The hyperpolarizability of newly designed and synthesized EO chromophores was measured by hyper-Rayleigh scattering (HRS) technique, and the discernible improvement in the hyperpolarizability for the new EO chromophores was found. Advantages of the new EO chromophores are also discussed.

1 Introduction

The electro-optic effect is the change in refractive index of a material induced by the presence of an electric field. The linear electro-optic (EO) effect is also known as Pockels effect. The EO effect is used in optical modulators and switches, which are key components of optical communications. It is expected that organic electro-optic (EO) polymers will be used in a wide variety of applications such as ultra-high-speed optical modulators and switches, high-speed digital signal processing, optical interconnection and optical sensors[1]–[5].

The EO effect is characterized by its optical modulation bandwidth f_{max} and figure of merit (n^3r) (n is the refractive index for optical wave and r is the electro-optic coefficient). EO polymers generally have low dielectric constants at microwave frequencies for modulation, and so the difference between the effective refractive index for optical wave and effective refractive index for microwave modulation is small, enabling ultra-high-speed modulation at a speed of or in excess of 100 GHz. Therefore, as far as the optical modulation bandwidth f_{max} is concerned, it does not matter for EO polymers.

On the other hand, the figure of merit (n^3r) is an index of EO performance at low voltage operation. This paper will first present a formula of r for EO polymers and then discuss how to improve the hyperpolarizability (β), which is one of its important parameters.

2 Design and evaluation of EO chromophore

2.1 Electro-optic coefficients of EO polymers

Figure 1 shows a schematic for EO polymers. Here, a side chain polymer, which is a polymer with an EO chromophore as the side chain, is shown as a typical example. The EO effect is a kind of second order nonlinear optical effect and does not exist in systems with inversion

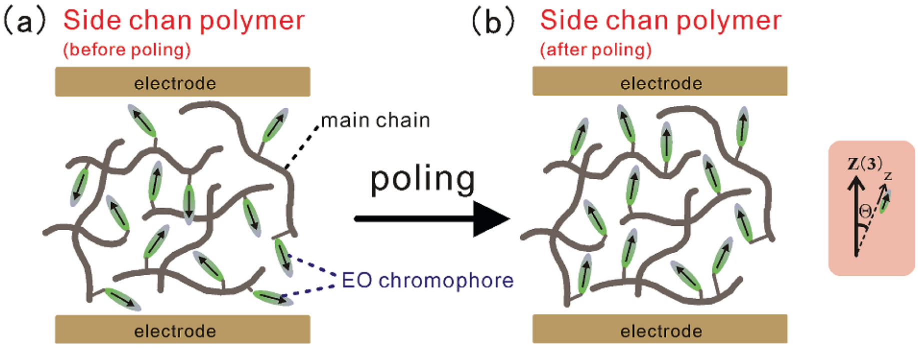

Fig. 1 Schematic for EO polymers

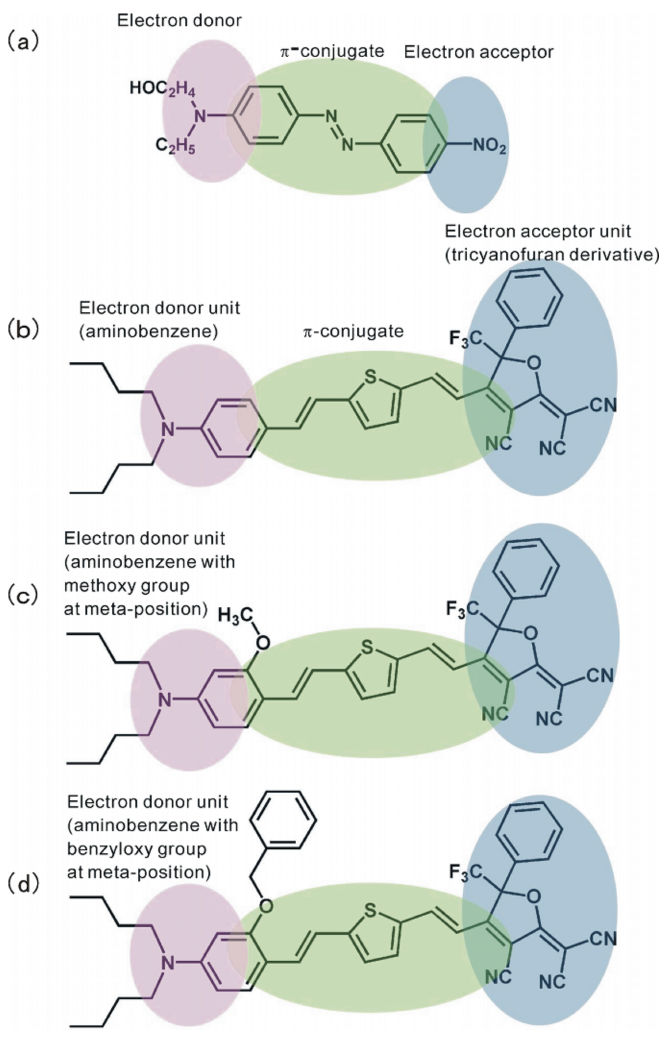

Fig. 2 EO chromophores used for this research

symmetry. Therefore, the EO effect is not generated in conditions such as (a) in Fig. 1, but generated in conditions such as (b). In order for the conditions of (a) to become the conditions of (b) the polymer usually experiences a poling process. More specifically, during this poling process, the polymer is heated to a near glass-transition temperature at which a relatively high electric voltage is applied to align the orientation of dipoles of EO chromophores and then the temperature is lowered to freeze that orientation.

$$r_{33} = -\frac{2}{n^4} L\, N_0 < \cos^3 \Theta > \beta_{zzz,\,EO} \qquad (1)$$

Equation (1) explains r_{33}, which is an important component of the electro-optic coefficient (r)[6]. In order to improve r_{33}, the number of EO chromophores per unit volume (N_0) must be increased, the orientation of EO chromophores must be aligned ($<\cos^3\Theta>$ must be increased) and the hyperpolarizability of EO chromophore (β_{EO}) must be enhanced. L is a collective representation of local field factors, which is not discussed in this paper.

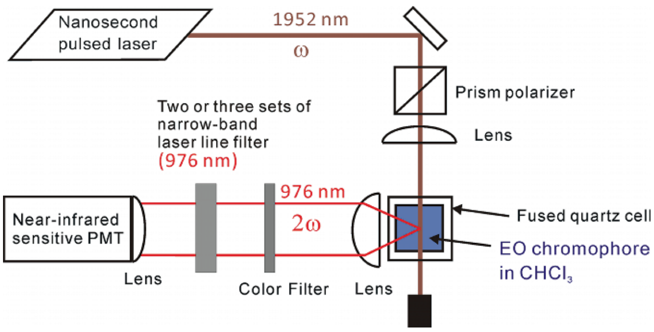

Fig. 3 Optical setup of hyper-Rayleigh scattering (HRS) measurements

In fabricating electro-optic devices, these parameters are not independent one another but are related in a very complex manner. This paper discusses the molecular design of EO chromophores to improve their hyperpolarizability (β_{EO}) and methods of measuring hyperpolarizability.

2.2 Molecular design of EO chromophores

Sample (a) shown in Fig. 2 is a typical EO chromophore, known as DR1. Typically, EO chromophores have an asymmetric structure (D-π-A) consisting of an electron donor unit (D), an electron acceptor unit (A), and a π conjugation system. Sample (b) is an EO chromophore developed by a group at the University of Washington that has extremely high hyperpolarizability. It consists of a tricyanofuran derivertive-based electron acceptor unit, an amino-benzene-based electron donor unit and a thienyl-di-vinylene-based π conjugation system. The development of the tricyanofuran derivertive-based electron acceptor unit was a particularly significant breakthrough in EO chromophore development[7][8]. Samples (c) and (d) are examples of new EO chromophores desgined and synthesized by NICT. Samples (c) and (d) have identical acceptor units and π conjugation systems, however they have amino-benzene with an alkyloxy group (methoxy group (OCH_3), benzyloxy group (OCH_2Ph)) at the meta-position as the donor unit.

2.3 Evaluation of EO chromophore hyperpolarizability

The hyperpolarizability of EO chromophores (β_{EO}) is a value that means the electro-optic response of a single molecule. The hyper-Rayleigh scattering (HRS) method was used to determine this value[9]. Figure 3 shows the optical setup of HRS measurements. In this method, a fundamental light comprising a pulsed laser impinges on the EO chromophore solution to detect second harmonic

Table 1 β values and maximum absorption wavelength (λ_{max}) of EO Chromophores

Sample	β_{HRS}(@1952nm)	β_{zzz}(@1952nm)	β_0	β_{EO}(@1.55μm)	λ_{max}[nm]
(a)	22.3	53.8	37.8	45.1	488
(b)	1090	2630	798	1310	780
(c)	1570	3790	922	1610	819
(d)	1660	4010	950	1670	823

unit for β: $\times 10^{-30}$ esu

light scattering (HRS light), which is caused by the temporal and spatial orientational fluctuation of the EO chromophore in the solution.

$$\beta_{HRS} \equiv \sqrt{\langle\beta^2_{HRS}\rangle} = \sqrt{\langle\beta^2_{HRSsolute}\rangle} \quad (2)$$

HRS intensity ($I_{HRS,2\omega}$) given as equation (2) is proportional to the square of fundamental light intensity (I_ω), proportional to the square of the hyperpolarizability of the solute molecule and also proportional to the concentration of the solute molecules (N_{solute}). The term related to the solvent in equation (2) is negligible in this research. Therefore, if there is a reference molecule with a known hyperpolarizability (in this experiment, DR1 of sample (a))[10], the hyperpolarizability (β_{HRS}) of the sample molecule can be determined by comparing the HRS intensity of reference molecule solution and sample molecule solution.

$$I_{HRS,2\omega} = g\left(N_{solvent}\langle\beta^2_{solvent}\rangle + N_{solute}\langle\beta^2_{solute}\rangle\right){I_\omega}^2 \quad (3)$$

In the actual measurements, the influence of multi-photon excitation fluorescence was estimated by frequency domain measurements because the contributions of HRS light and multi-photon excitation fluorescence in the detected signal overlap. Table 1 is a summary of HRS measurements using fundamental light with a wavelength of 1952 nm. The chloroform solution of samples (a), (b), (c) and (d) was used for HRS measurements. Various β values in Table 1 are given as the below equations.

$$\beta_{HRS} \equiv \sqrt{\langle\beta^2_{HRS}\rangle} = {}^6/_{35}\,\beta_{zzz} \quad (4)$$

$$\beta_{zzz} = \frac{\omega^4_{eg}}{(\omega^2_{eg}-4\omega^2)(\omega^2_{eg}-\omega^2)}\beta_0 \quad (5)$$

$$\beta_{EO} = \frac{\omega^2_{eg}(3\omega^2_{eg}-\omega^2_{EO})}{3(\omega^2_{eg}-\omega^2_{EO})^2}\beta_0 \quad (6)$$

Here, ω_{eg} represents angular frequency between excited and ground states that is readily calculated by the wavelength at the maximum value of the absorption spectrum. β_0 is the value of β_{zzz} at the zero-frequency. ω_{EO} is an angular frequency of the optical wave (1.55 μm) and β_{EO} is the corresponding hyperpolarizability. The dominance of the β_{zzz} component for EO chromophores and the two-state model was assumed[11]. Thus, the value of β_{EO} can be determined using HRS measurements.

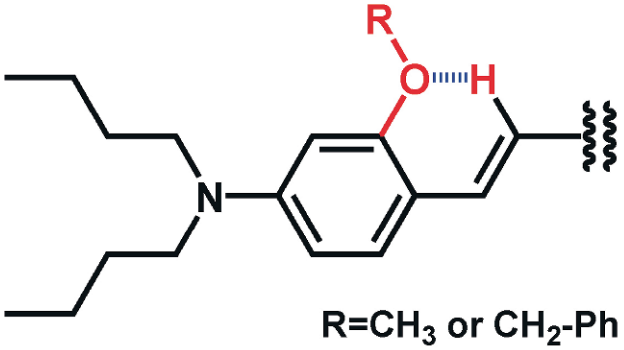

Fig. 4 Intra-molecular weak hydrogen bonding of EO chromophores with an alkyloxy group

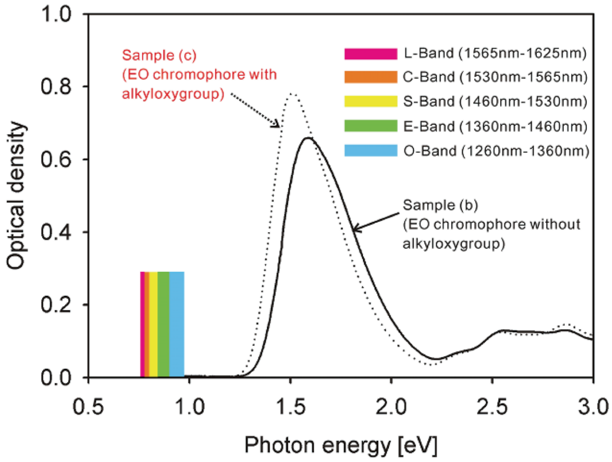

Fig. 5 Absorption spectrum of EO chromophores without alkyloxy group (sample (b)) (solid line) and with alkyloxy group (sample (c)) (dotted line)

2.4 Characteristics of EO chromophores with an alkyloxy group

As shown in Table 1, EO chromophores with an alkyloxy group exhibited a β_{EO} value 1.3 times greater than those of EO chromophores without an alkyloxy group. We think that this increase originates from the intra-molecular weak hydrogen bonding as shown in Fig. 4 suppressing the dynamical fluctuation of π conjugation systems, which contributes to the structural stabilization, resulting in elongation of the effective π conjugation length. We think that large molecules as shown in Fig. 2 have high degrees of freedom and therefore the structures fluctuate at a given environment. The existence of intra-molecular weak hydrogen bonding as shown in Fig. 4 is also suggested by the proton nuclear magnetic resonance spectrum (^{1}H-NMR) [12].

Figure 5 shows the absorption spectra in the chloroform of samples (b) and (c). Compared to EO chromophores without an alkyloxy group, the absorption band of the EO chromophores with an alkyloxy group shifted toward a low energy (long-wavelength) region with narrower absorption bandwidth. The change of the slopes in the low energy region in the absorption band mainly contributes to the narrowing of the absorption band. We think this also originates from intra-molecular weak hydrogen bonding. The chromophore does not only have a large β_{EO} value but the aforementioned characteristics of the absorption spectrum have great advantages when fabricating EO devices using this chromophore. Generally, a trade-off relationship between the value of β_{EO} and the absorption wavelength exists. The absorption bandwidth in sample (c) is narrower and particularly, a low energy region of the absorption band sharply decreases. This indicates that it has potential to reduce propagation loss due to absorption.

This paper only discusses EO chromophore with a thienyl-di-vinylene-based π conjugation system, however we have also confirmed the effect of intra-molecular weak hydrogen bonding due to the alkyloxy group in EO chromophores with long π conjugated systems such as polyene and phenyl-di-vinylene. Therefore, this approach, that is, addition of methoxy or benzyloxy groups to meta-positions of the amino benzene donor, is an important area of progress in the design of EO chromophores[12].

3 Conclusions

There have been a number of reports that the figure of merit (n^3r) of EO polymers has greater value compared to the figure of merit of $LiNbO_3$, a typical inorganic EO material. It is expected that the development of new EO chromophores as discussed in this paper and controls of molecular orientation will further improve their figure of merit. As EO polymers have low dielectric constants at microwave frequencies, they are also superior to $LiNbO_3$ in terms of modulation bandwidth. While the development process, heat resistance, lifetime and other properties still need to be improved and enhanced, we believe EO polymers are promising.

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