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Progress toward Device-Quality Second-Order NLO Materials: 3. Electrooptic Activity of Polymers Containing *E*,*E*,*E*-[4-(*N*,*N*-Dialkylamino)-phenyl]pentadienylidene-3-phenyl-5-isoxazolone Chromophores

Fang Wang, Aaron W. Harper, Michael S. Lee, and Larry R. Dalton*

Loker Hydrocarbon Research Institute, Departments of Chemistry and of Materials Science & Engineering, University of Southern California, Los Angeles, California 90089-1661

Hua Zhang, Antao Chen, and William H. Steier

Center for Photonic Technology, Department of Electrical Engineering, University of Southern California, Los Angeles, California 90089-0430

Seth R. Marder

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

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Recently, electrooptic (EO) devices, fabricated from organic chromophore containing polymeric materials, have been shown to yield operational bandwidths greater than 100 GHz, to operate with digital level (<5 V) drive voltage (V_π) inputs, and to exhibit good operational stability.[1–4] Also, significant improvements in chromophore hyperpolarizability and thermal stability have recently been realized.[5–8] Despite these advances, there are still very few materials which fulfill all of the requirements for device applications. Because of the nonlinearity/transparency tradeoff, most of the EO materials which possess an electrooptic coefficient greater than that of $LiNbO_3$ (30 pm/V at 1.3 μm) have an absorption maximum greater than 600 nm. Such absorption can result in high optical losses at diode wavelengths (630−980 nm). Due to the increasing interest in diode-wavelength modulator applications, the search for so-called blue-shifted chromophores has been receiving increasing attention.[9]

Marder et al.[10] and Jen et al.[11–14] have demonstrated that chromophores containing polyene segments and thiophene rings yield much larger nonlinearities than

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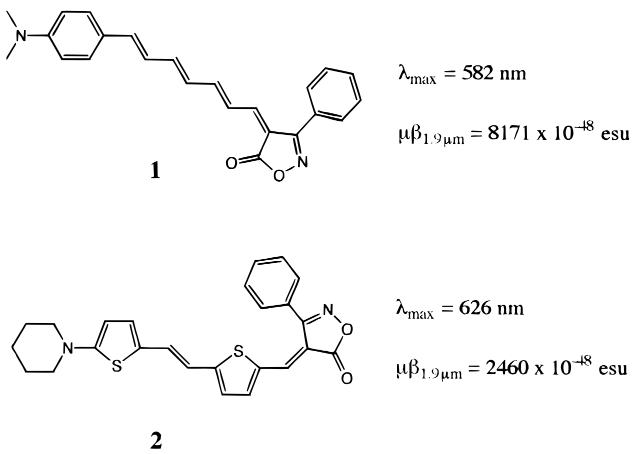

Figure 1. Comparison of related polyene- and thiophene-bridged chromophores **1** and **2** of comparable conjugation lengths.

conventional chromophores that have strongly aromatic ground-state structures, e.g., those containing stilbene bridges.[7,8,10−17] It is believed that for molecules containing multiple phenyl groups, the aromatic stabilization in the neutral canonical resonance form will hinder charge separation and consequently lead to large values of bond length alternation and diminished nonlinearities.[15] Chromophores with conjugated polyene bridges have also been shown to give more satisfactory results in terms of nonlinearity/transparency tradeoff than those with thiophene bridges. For example, the absorption maximum of compound **1** is more than 40 nm blue-shifted than that of compound **2**, although its dipole moment−hyperpolarizability product is more than three times larger (see Figure 1).[8,14]

A major challenge in the design of nonlinear optical chromophores for electrooptic (EO) devices is simultaneously achieving acceptable thermal stability, optical transparency, optical nonlinearity, and processability in one compound. Although the thermal stability of long conjugated polyene-based chromophores should be of concern, relatively shorter polyene-based chromophores, which give reasonable thermal stabilities and optical nonlinearities, are candidates for electrooptic materials. In light of this, we chose to incorporate *E,E,E*-[4-(*N,N*-dialkylamino)phenyl]pentadienylidene-3-phenyl-5-isoxazolone chromophores (**3** and **4**) into polymer thin films and evaluate their potential as electrooptic materials.

Chromophore **3** (see Figure 2) was first reported by Marder et al.[10] This chromophore possesses a hyperpolarizability of $\beta_0 = 218 \times 10^{-30}$ esu, and an absorption maximum of 564 nm ($CHCl_3$). Despite the advantageous nonlinearity/transparency ratio, there are no reported electrooptic coefficients of materials derived from this chromophore. To improve the solubility of this chromophore in polymer hosts, we prepared the analogous chromophore **4**, *E,E,E*-[4-(*N,N*-diethylamino)phenyl]-pentadienylidene-3-phenyl-5-isoxazolone (denoted as APTEI) in which the methyl groups on the donor nitrogen were replaced with ethyl groups. In addition to a dramatic increase in solubility, the absorption maximum experienced a red shift of 22 nm compared to chromophore **3**. Using the well-known relationship between band gap and optical nonlinearity, this red shift corresponds to a hyperpolarizability of $\beta_0 = 254 \times 10^{-30}$ esu, which is ∼20% larger than that of chromophore **3**. This increase in optical nonlinearity due to donor substituent modification was to be expected, as examples can be found in the literature that show such enhancement in nonlinearity by simply replacing the two methyl groups on the nitrogen with longer alkyl groups.[18] Poly(methyl methacrylate) doped with APTEI, as well as thermosetting polyurethanes derived from difunctionalized and trifunctionalized analogues of this chromophore were prepared and evaluated for use as electrooptic materials.

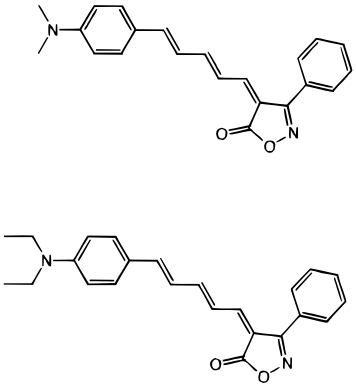

Figure 2. Structures of the literature chromophore **3** and the modified analogue APTEI **4**.

Table 1. Electrooptic Coefficient (r_{33}) and Refractive Index for APTEI/PMMA Composites versus Loading Density

loading density (wt %)	r_{33} (pm/V)	*n*, refractive index
10.3	36.2	1.55
20.6	49.2	1.62
30.9	40	1.69
41.2	39.9	1.74

Polymer composites of APTEI were prepared by codissolving the chromophore with PMMA in 1,2-dichloroethane. The resulting solution was filtered through a 0.2-μm syringe filter, and subsequently spin-cast onto indium−tin oxide coated glass substrates. After drying in vacuo, each film was corona poled under the application of a 6 kV potential applied to the needle positioned 2 cm above the film. Poling temperature was adjusted to achieve the largest possible second-harmonic signal. Electrooptic coefficients were obtained at 1.06 μm using modified electric field modulated attenuated total reflection spectroscopy, in accord with Chen et al.[19]

Table 1 lists the electrooptic coefficients and refractive indices of APTEI/PMMA composites at different loading densities. A high r_{33} of 49 pm/V was achieved with 20 wt % chromophore loading in PMMA. The calculated

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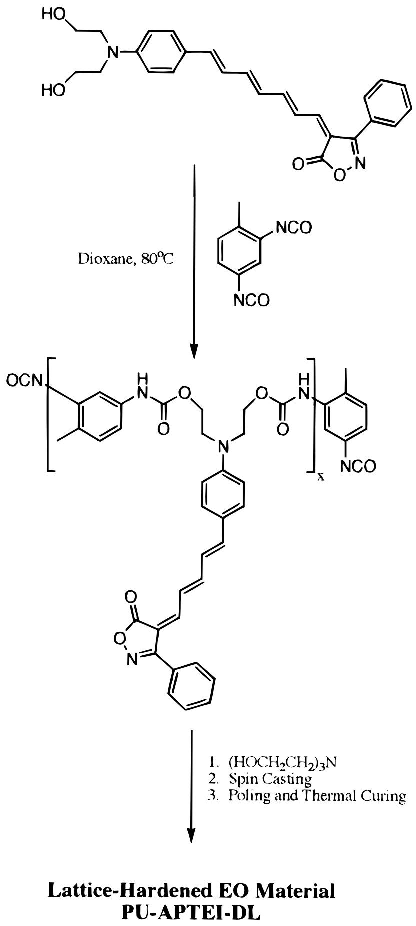

Figure 3. Preparation of a thermoset electrooptic polymer with the covalent incorporation of APTEI.

r_{33} at 1.3 μm (using the two-level model[20]) is 39.4 pm/V, which is somewhat larger than the EO coefficient of $LiNbO_3$ at the same wavelength (31 pm/V).

The results from Table 1 are impressive when the nonlinearity/transparency tradeoff is considered. The APTEI/PMMA films are more than 50 nm blue-shifted from any other material of comparable electrooptic activity.[5-8] This advantageous electrooptic activity/transparency characteristic may allow APTEI-based materials to be used for diode-wavelength electrooptic applications. Also notable is the linear dependence of refractive index on loading density. Unlike the majority of composites containing high-$\mu\beta$ chromophores, the refractive index dependence on loading density remains linear, which indicates that the chromophores remained dissolved in the polymer matrix even at concentrations that normally lead to precipitation. That the chromophores remain dissolved in the polymer matrix at all loading densities examined suggests that the attenuation of electrooptic activity versus chromophore concentration is not due simply to chromophore precipitation, but rather to electrostatic intermolecular interactions which interfere with chromophore alignment during the poling process.[21-23] Statistical mechanical calculations explicitly treating intermolecular electrostatic interactions further support this view.

If an appropriate analogue of APTEI could be incorporated into a polymer matrix, such that the material exhibits electrooptic activities similar to the guest−host systems, as well as acceptable thermal and temporal stabilities of electrooptic activity, APTEI-based polymers may find utility in the development of devices operating in the digital volt range. To this end, we chose to covalently incorporate APTEI in a thermoset, poly(urethane)-like polymer.

The preparation of the thermoset polymer is shown schematically in Figure 3. The amounts of the chromophore, 2,4-toluene diisocyanate (TDI), and triethanolamine (TEA, the trilinker) used were chosen such that the hydroxy and isocyanate groups were stoichiometrically balanced, and the overall number density of chromophore corresponded to that which gave the largest electrooptic coefficient for the APTEI/PMMA composites. The processing procedure was as follows: The appropriate amounts of monomers were dissolved in dioxane and heated for 1 h at 80 °C, then TEA was added and heating was continued for another 15 min.

The resulting solution was filtered, spin-cast onto ITO-coated glass substrates, and dried in vacuo at room-temperature overnight. The films were then poled and measured using the same procedure as for the APTEI/PMMA composites, although with a stepped voltage/temperature protocol.[24]

The resulting thermoset polyurethane, denoted PU-APTEI-DL, possessed an electrooptic coefficient of 32 pm/V at 1.06 μm. This value is lower than that of the guest−host composite at the same chromophore loading density. This decrease in electrooptic activity is due to the decreasing mobility of the chromophore in the lattice as the cross-linking reaction progressed throughout the poling procedure. The dynamic thermal stability[25] of PU-APTEI-DL is shown in Figure 4. Because of the ease of using second-harmonic generation for continuously monitoring second-order optical nonlinearity as compared to more time-consuming electrooptic coefficient measurements, second-harmonic generation was used to monitor both the induction of electrooptic activity by poling and the assay of thermal stability of that activity after the poling field was removed. By "dynamic thermal stability", we mean the measurement of the loss of second-order nonlinear optical activity in a thermal ramping experiment analogous to thermal gravimetric analysis. The temperature at which optical nonlinearity is first observed to decrease is taken as defining the thermal stability.

From Figure 4, it can be seen that PU-APTEI-DL possesses excellent thermal stability of electrooptic activity to 78 °C, which is slightly lower than that of the similar, well-known PU-DR19 thermosetting material.[26] Although it should be noted that the thermal stability shown here does not represent that of a

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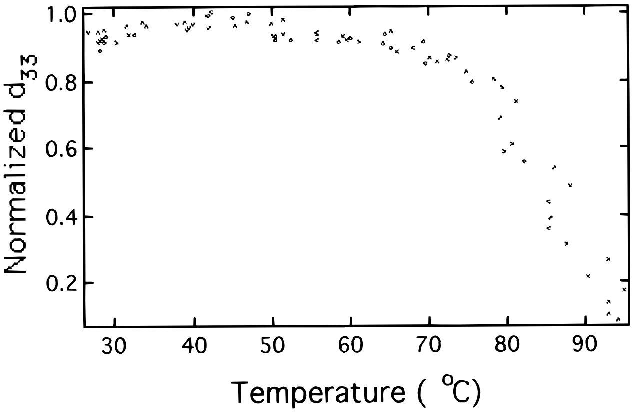

Figure 4. Dynamic thermal stability of second order nonlinear optical activity for PU-APTEI-DL material is shown. Because of the ease of continuously monitoring second-harmonic generation as compared to measurement of electrooptic activity, second-harmonic generation was monitored as the temperature was continuously increased at a rate of 10 °C per minute.

carefully optimized processing protocol, experience with similar systems suggests that careful investigation of poling and cross-linking conditions can elevate the thermal stability upward of 90 °C. Nevertheless, PU-APTEI-DL as shown here may find utility in those applications where device processing, use, and storage temperature requirements are less stringent.

Very recently, we have observed that replacing the 3-phenyl-5-isoxazolone acceptor with a cyanofuran acceptor and protecting the polyene bridge with bulky groups such as the isophorone group leads to materials with significantly improved electrooptic activity and thermal stability.[27] Electrooptic coefficients (at 1.06 μm) on the order of 100 pm/V have been measured for composites of these chromophores in PMMA. Material optical loss values typical fall in the range 0.8−1.1 dB/cm at 1.3 μm measurement wavelength suggesting that chromophore interband absorption does not contribute to loss. With such materials, Mach−Zender interferometers with drive voltage requirements of less than 1 V have been fabricated (compared to 4−5 V requirements for lithium niobate modulators).[28] These results reinforce the above conclusions concerning the utility of polyene bridge structures. The results also emphasize the role of inert substituents in improving solubility and inhibiting unwanted intermolecular electrostatic interactions that attenuate poling efficiency.[27]

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