Overview of EO Polymers and Polymer Modulator Stability

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ABSTRACT

This is a brief overview of the technology of nonlinear optical polymers (NLOP) and their use in electro-optic (EO) modulators. This paper also covers preliminary results from the authors' laboratories on highly active CLD- and FTC-type chromophores in guest-host films of APC amorphous polycarbonate. Emphasis will be given to thermal stability and long-term EO modulator aging.

1. INTRODUCTION

For years device engineers have been interested in electro-optic modulators based on nonlinear optical polymers because of their ease of processing and rugged flexibility, and now even more so for the promise of exceedingly high electro-optic coefficient (r_{33}). Recent reports say that films of third-generation organic chromophores exceed lithium niobate (LN) by a factor of ten in electro-optic (EO) coefficient ($r_{33} \approx 300$ pm/V versus 30 pm/V for LN) [1]. Thin film processing knowledge is accumulating [2]. New methods for fabricating high-quality waveguides and integrating light sources have been reported [3]. But the first question device engineers ask is "how stable are those materials?" This paper reviews current EO materials technology, and gives data on the thermal stability of guest-host EO films and oven-aged EO modulators.

1.1 First-generation materials

The first generation of organic electro-optic modulator films, reported 20 years ago, were made by "doping" (i.e., dissolving) small, well-known dyes, such as Disperse Red 1 (DR1) and diaminonitrostilbene (DANS), in host polymers such as poly(methyl methacrylate) (PMMA). The small size of the dyes (called chromophores hereafter) and the low softening temperature of the host polymer (110 °C) resulted in fairly noticeable decay of the electro-optic coefficient at temperatures above 50 °C. Attaching the chromophore as a side-chain to the polymer added thermal stability. One of the pioneering teams in this field aged a side-chain DR1-PMMA EO modulator for 7.5 years at room temperature and found the r_{33} had decreased only 30% (equivalent to the V_{π} increasing from 5 to 7 volts) [4]. The same team 13 years ago reported the fabrication of a 40 GHz polymer modulator [5]. These EO films were not thermally stable enough for many applications. Furthermore, they had about half the electro-optical coefficient of lithium niobate at 1550 nm. However, the ease of processability and capability for high bandwidth kept incentive high for developing better EO polymers, that is, until the photonics-boom bubble burst in the late 90's and dampened the commercial development stampede.

1.2 Second-generation materials

Several R&D groups reinvigorated the community with the synthesis of second-generation chromophores, such as CLD and FTC, reported in the late 1990's [6]. Important milestones were the demonstration of sub-one-volt V_{π} modulators with a low-loss CLD/PMMA guest-host material reported in 2000 by Shi [7],

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and the demonstration of 110 GHz modulation in a polymer EO material [8]. Improvements were made in thermal stability of guest-host films by using polycarbonates and polyimides with higher glass transition temperatures (205 to 250) °C. The Lockheed-Martin group made important strides with their FTC chromophore (called 46M) as a guest in high T_g host polymers. In 2000 they reported an EO modulator with 25% 46M in APC amorphous polycarbonate that had less than 2 dB/cm propagation loss, a single-arm V_π of 2.4 volts and maintained V_π at 2.4 volts for over 4000 hours of operation [9].

Useful quantities of the CLD-1 chromophore are now commercially available from Aldrich [10]. However, we have found that making high quality films from CLD-1 in 1,2-dichloroethane requires finding a very narrow window of processing conditions. The NAVAIR-China Lake group has developed guest chromophores that contain bulky groups. The bulky groups enable the chromophores to have several months of pot life in the spinning solutions, high solubility in host polymers, and negligible sublimation during poling at 150 °C. The chemical structures of these materials will be reported elsewhere. Preliminary stability data is presented below.

1.3 Third-generation materials

Third generation chromophores (with higher β) are currently under development in several laboratories [11, 12, 13]. The main strategies for increasing the electro-optic coefficient of an organic EO material are: (1) increasing the molecular hyperpolarizability (β), (2) increasing the degree of polar alignment, and (3) increasing the chromophore concentration. Larger β usually brings with it larger dipole moments. Therefore, new molecular architectures are being explored to alleviate dipole-dipole repulsion to enable closer packing of the larger dipoles. Attaching bulky groups to the sides of chromophores greatly diminishes anti-polar pairing during poling [14]. This allows one to increase the concentration of polar-oriented chromophores in the film until the total volume of the bulky groups becomes the concentration-limiting factor. Tying three or more chromophores together in a branched structure (a dendrimer) is another motif being explored at the University of Washington [15]. All of these efforts are forming the foundation for truly revolutionary third-generation organic EO materials.

1.4 Limits to organic chromophore development

Kuzyk's group has reported a quantum mechanical upper limit to the molecular first hyperpolarizability, β, for organic chromophores [16], which has not yet been reached. Low optical loss is just as important as having a high electro-optic coefficient. Therefore, a more important figure of merit is β/α where α is the molar absorptivity at the operating wavelength. There may be a limit to the size of future chromophores for operating in the near infrared (NIR) band (1300 – 1550 nm), because, in general, larger chromophores have a more red-shifted electronic absorption resonance. For some high-β redshifted chromophores the tail of the electronic resonance can be seen absorbing a bit at 1300 nm (but still negligible electronic absorption at 1550 nm). Some degree of red shifting may be acceptable if the increase in r_{33} allows one to decrease the length of the modulator arms to offset the increase in attenuation (dB/cm) and maintain the same V_π -- miniaturization drives many applications. However, in general, electronic absorption should be avoided for long-term stability because it may lead to photolytic chromophore degradation.

Our laboratory uses a solution technique to measure the absorption loss of new EO materials (200 mgs of material is required). Numbers from this screening procedure were about 1.0 to 1.5 dB/cm lower than what was measured in poled buried waveguides. As a rough rule of thumb, the loss due to the chromophores electronic absorption should be kept below 1 dB/cm (at the concentration used in the waveguide). This is because there are other optical loss mechanisms that are difficult to eliminate and each one typically adds a few tenths of a dB/cm attenuation. These are: (1) absorption due to carbon-hydrogen vibronic-resonance overtones (and other NIR overtones and combination bands); (2) light scattering off sidewall roughness and other processing defects; and (3) electric-field poling (which can be kept under 0.5 dB/cm depending on the voltage used).

The second-generation chromophores (like CLD) already require more than a half-dozen synthetic steps. Synthetic procedures and purifications for the 3rd generation chromophores are approaching the complexity of many large biological macromolecules. But synthetic complexity should not be a limiting factor because the cost of the chromophore is a small fraction of the cost of the device.

1.5 Stabilizing organic EO materials by chromophore attachment

The easiest way, but least stable way, to implement a new EO material is in the guest-host motif (chromophore dissolved in a polymer), and these materials will be covered in detail in sections 2 & 3 below. For higher stability the chromophore can be attached as a side-chain to a high Tg polymer [17]. The present authors are exploring EO side-chain core materials and these will be reported elsewhere [18]. The reason side-chain attached materials lag behind the guest-host materials has been that, until now, either the r_{33} or the optical loss (or both) are not quite as good as the guest-host materials offer. Furthermore, the learning curve for modulator fabrication requires lots of material, and large quantities of the guest-host materials are more readily available. We believe, however, that the side-chain materials will prevail with a little more effort in tailoring the structures, and after gaining the processing know-how. Crosslinking the EO materials are another good stabilizing strategy that will be reviewed in Section 4 below.

1.6 Eliminating stability issues during film processing

The chromophore defines the limits of stability (it is the weak link). The baking and poling temperature (or rather time-temperature integral) must not exceed the onset of decomposition conditions for a particular chromophore. The worst possible conditions are the combination of oxygen (air), light (especially fluorescent room light), and elevated temperature. High-activity chromophores must be poled in an inert atmosphere and in a yellow or red darkened room. More will be said about this in section 4.3 below.

During the poling operation, the core and cladding polymers are subject to high voltages (e.g., 120 volts/micron) lasting an hour or more at high temperatures. If the poling voltage is too high, it may be possible for electrochemical reactions to occur that degrade the chromophore and reduce the EO coefficient, but this would be very unlikely unless ionic impurities are present (or at very high chromophore loadings where electron or hole tunneling may occur). Under normal service conditions the EO modulator operating voltage is quite low (< 0.5 volts/micron). However, long-term modulator operation using a single direction of polarity across the film (or a dc bias) can cause ionic impurities to drift towards the electrodes, and that may cause the operating voltage to change over time. Hence, purity of the materials is of utmost importance.

2. THERMAL AGING OF GUEST-HOST EO MATERIALS

2.1 Background

The thermal stability of the EO coefficient of guest-host film at a given temperature depends primarily on how far below the glass transition temperature of the blend one carries out the test (assuming the chromophore itself has adequate chemical stability at that temperature). This is because as the T_g is approached, free volume increases and the chromophores undergo accelerated rotation. For guest-host EO films, as more chromophore is dissolved in the polymer, the glass transition temperature is depressed creating a trade-off between thermal stability and EO coefficient. As a rule of thumb, for second-generation guest-host core materials, the softening temperature of the film must be at least 70 °C higher (preferably 100 °C higher) than the long-term operating temperature of the modulator to maintain a low operating voltage for many years. Larger chromophores, and especially chromophores chemically attached to the matrix, would have a less stringent rule of thumb.

The basic structure of CLD contains an isophorone-unit, and the FTC-type chromophore contains a thiophene unit in place of the isophorone. Both chromophore types are well known by now and both were used in the present study. We found that certain bulky groups attached to these chromophores impart the following beneficial properties: (1) increased pot-life of concentrated spin-casting solutions, (2) increased solubility of chromophores in the host polymers, and (3) elimination of chromophore sublimation during electric-field poling at 150 °C for 30 minutes. The highly soluble chromophores for guest-host core materials are herein called CLD-X, CLD-Y and FTC-X. The synthesis of our hydroxy-functional CLD precursor was published by Davis [19]. The synthesis of the CLD-X, CLD-Y and FTC-X chromophores will be reported elsewhere. The Corning group has also modified CLD- and FTC-type chromophores with different bulky groups to improve solubility [13, 20].

2.2 Quick methods to screen for thermal stability

In the present study, to ensure that the guest-host films did not suffer from sublimation of the chromophore and did not undergo chemical degradation due to oxidation and reaction with impurities in the polymer, a thin-film aging test was developed whereby changes in the UV-Vis-NIR spectra was monitored [21]. Changes in the absorption spectra were measured after 30 minutes at three temperatures. Measurements indicated less than 1% change at poling conditions.

Another quick screening method for thermal stability is to heat a poled film at 10 degrees per minutes while monitoring the r_{33} signal by the Teng-Man method (or monitor the second-harmonic generated). Oh, et al., used this method for a guest-host film of 30% CLD in APC polycarbonate and showed that the NLO coefficient held fairly constant till near 120 °C [22]. The T_g of APC is 205 °C, but dissolving 30% chromophore in the APC lowers the mid-point of the T_g to about 145 °C. At slower heating rates the roll-off temperature would have been lower. The T_g of the blend can be measured by casting and drying a thick film for use in a differential scanning calorimeter (DSC). Once the Tg of the blend is known, many predictive models are available that give a fair estimate of EO performance (V_π increase) as a function of time and temperature. But one still needs to carry out the oven-aging tests to determine the best fitting parameters for the model.

For guest-host core materials, one should be careful to stay below the solubility limit of the chromophore where it can become supersaturated. If the thermodynamic solubility limit is exceeded, long-term annealing at elevated temperatures can lead to phase separation, that is, the creation of two domains, one rich and one lean in chromophore (the rich on having a lower Tg and higher index of refraction). Another worst-case scenario would be the precipitation of small crystallites of chromophore that scatter light out of the waveguide. These situations can be screened by inspecting the annealed films with a polarizing microscope, or by observing thermal events after multiple DSC runs and careful annealing in the DSC.

2.3 Oven aging of EO modulators

The half-wave voltage of the modulator, V_π, is inversely proportional to the EO coefficient. As the polar order of the chromophore randomizes by rotational diffusion, the electro-optic coefficient will decrease and the V_π will increase. The relaxation of polar order is a very slow process at temperatures well below the Tg. The Tg of the polymer-chromophore blends reported here was about 140 °C.

Mach-Zehnder modulators were fabricated from the CLD-X and FTC-X guest-host core materials, and oven aged at three elevated temperatures. The data is summarized in Table 1. A model after Dissado-Hill [23] was used to fit the data and extrapolate to the out-years. Shortly after the temperature was increased, there was an initial rapid relaxation period (increase in V_π). This rapid relaxation might be due to the thermally stimulated discharge of trapped charges, rotation of a fraction of chromophores that lie adjacent to thermally expanded nanovoids (those that immediately became large enough to accommodate the chromophores rotation), and other unknown mechanisms. There is DSC evidence that the FTC-X/APC film, which had 35% chromophore loading, may have exceeded its solubility limit causing a phase separation in which the Tg of one of the two phases was less than 100 °C.

The relaxation rate at longer times (years) is coupled to the rate of polymer chain relaxations at the size scale of the chromophore. A plot of actual data taken with modulators made from the CLD-X/APC is shown in Figure 1. As the temperature approaches Tg, the increase in V_π with temperature accelerates as 1/(Tg-T).

Table 1. Oven aging of modulators: V_π vs. time and temperature

	Half-wave voltages			
Core type	1hr	1mo	5yrs	10yrs
CLD-X / APC (a polycarbonate obtained from Aldrich)				
80 °C	5	11	17	19
95 °C	5.5	14	21	23
110 °C	5.5	34	52	56
FTC-X / APC				
80 °C	7.3	13	21	23
110 °C	6.8	57	91	98

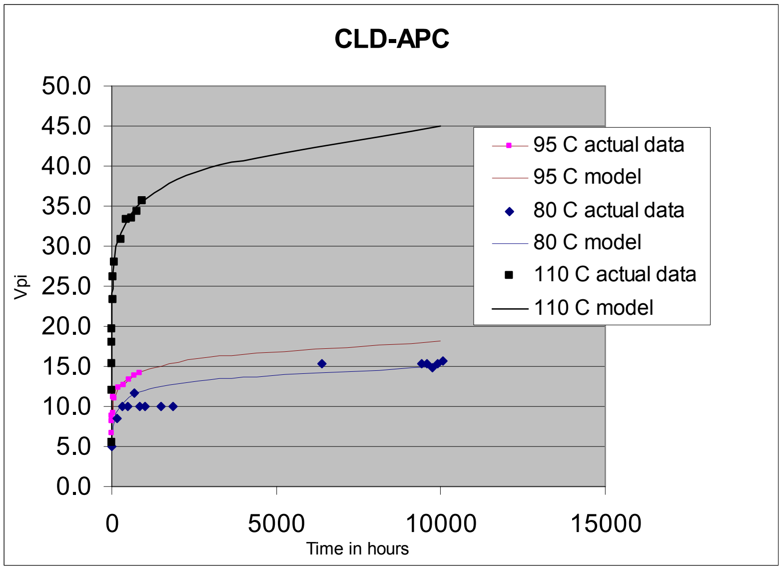

Figure 1. Modulator V_π as a function of time at three temperatures.

2.4 Annealing and physical aging

For the present study, this was not done, but a study by Shen and Wong showed that if an EO polymer modulator is annealed for about 20 hours at the highest temperature desired for modulator operation while applying the poling electric field, the short-term relaxation of polar order (6 hours after poling) can be diminished by a factor or 1.4 [24]. This is due to the physical aging process. When a polymer is cooled from the melt below the glass transition temperature, transient free volume is kinetically trapped in the material such that the density of the material only slowly increases over a period of many hours. As the free volume dissipates, the equilibrium density for that temperature is approached (but never reached). Holding the chromophores erect with the applied field while the bulk material densifies around it helps retain more of the polar order after the field is released. However, after annealing, if the sample is heated above that annealing temperature, the effects of annealing and physical aging are partially erased.

4. OHER AGING AND STABILITY CONSIDERATIONS

4.1 Stability of side-chain polymer EO systems

For increased thermal stability, chromophores should be chemically attached to polymer backbones. This obviates the solubility problem and makes it easier to increase the Tg. The reports on side-chain EO polymers are too numerous to review here; however, however results from a few recent reports are summarized in Table 2 [17, 18, 25-29].

Table 2. Normalized EO aging data

EO Core Material[a]	Temperature	Time	% retention	Reference
PI-DCV-azo	100 °C	1,000 hrs	95%	26
PI-SO_2CN-azo	100	600	92	27
PQ-diCN-ene	85	1,100	93	28
PI-NO_2-azo	80	25	89	25
35%CLD-X/APC	80	10,000	45	this paper
25% CLD-1/APC	60	1,560	83	29

[a] PI = polyimide; PQ = polyquinolin; the appended acronyms are well-known chromophores

Even though many reports show 100's of hours of stability at 100 °C, side-chain EO polymers have not yet obviated the guest-host EO materials. As the dramatic improvements in the EO coefficient, r33, begin to mature, more and more emphasis will be place on thermal stability and optical loss, and more work will be focused on developing the attached-chromophore motifs.

The Tg of side-chain EO polyimides in the authors' laboratories was tailored to be about 175 °C, partly because that is a safe temperature to pole the CLD chromophore [18], but also because it is believed that a Tg of 175 °C will provide adequate modulator longevity (e.g., 10 years useful life at 100 °C) for most applications now envisioned.

4.2 Stability of crosslinked EO systems

Crosslinking the polymer/chromophores during the poling process may give the most thermally stabilized EO film, however this is difficult to achieve in practice since it must be carried out during or after the poling operation [30, 31]. Some progress has been made in crosslinked sol-gel organic hybrid EO core materials [32, 33]. Layer-by-layer crosslinking of self-assembled chromophores has been reported by the Marks group at Northwestern University, and it shows promise for developing very thermally robust modulator films [34].

Our laboratory has found that adding a few percent of a difunctional crosslinking agent to an appropriately functionalized chromophore-containing polymer and thermally curing it eliminates solvent damage to the film. Work on cross linking EO films during the poling operation by this method will be reported at a future date.

4.3 Photo-oxidation stability

Generating data on the photo-stability of these materials is an equally important data base in need of additional attention. Zhang, et al., have shown that elimination of air (oxygen) greatly enhanced photo stability of a CLD-1/APC modulator [29]. With air exposure the modulator response dropped about 60% in 20 hours, whereas under argon-gas protection no drop in power was observed in 120 hours (operating at an optical wavelength of 1550 nm and 10 mW input power). Other studies have found similar behavior with other chromophores [35].

We have found that the FTC-type chromophore is more resistant to degradation than is the CLD-type chromophore. The molecular hyperpolarizability (β) of FTC is lower than that for CLD. However, the lower β can be compensated for by poling with a higher electric field because our FTC-X can tolerate higher poling fields than CLD-X without incurring more optical loss. The CLD-type chromophores have 4 allylic-hydrogens on the isophorone group, whereas in FTC-type chromophores the isophorone is replaced by a thiophene group that has no allylic hydrogen. The only deficiencies our laboratories have found with the FTC chromophore is that it is harder to photobleach (a preferred method to pattern the waveguide).

Absorption of light by a chromophore can promote a π-electron to a higher energy state and can generate a free radical that can react with another chromophore and slowly degrade performance over time. Hence, the addition of commercially available radical scavengers (anti-oxidants), and light stabilizers (hindered amine light stabilizers, HALS [34]) will be part of future programs to further increase the stability of organic EO modulators. One study has shown success in the use of DABCO (bicyclo(2, 2, 2)-1, 4-diazaoctane), a singlet quencher, to protect the chromophore against photo-induced degradation [36].

4.4 Radiation stability

There is a host of polymer literature on the effects of various types of radiation on the physical properties of polymers, which will not be reviewed here [37]. The outcome of exposure to radiation depends upon the chemical structure of the material exposed, the type and intensity of the radiation, the presence and amounts of oxygen, water, radical scavengers, impurities, stabilizers, etc. The exposure of polymers and organic materials to actinic radiation can generate reactive free radicals that abstract hydrogen from carbon atoms causing further reactions. Some types of polymers, like poly(methyl methacrylate), PMMA, will undergo chain scission when exposed to an electron beam [38]. Chain scission would lead to accelerated relaxation of the EO coefficient. In other types of organic materials beneficial combination reactions can occur leading to crosslinking of the polymer matrix. It is mandatory to do the testing because it is difficult to predict the outcome.

The earliest study of radiation effects on EO polymers was reported on PMMA/DR1 and main-chain EO polymer films exposed to gamma radiation (up to 44 MRad) [39]. No degradation of the nonlinear optical properties (as measured by SHG) was observed for the main-chain EO polymer, while the PMMA/DR1 SHG signal diminished about 35% on average. In a recent study by Taylor, et al., only small effects due to proton and gamma-ray exposure on the performance of polymer optical modulators made from polycarbonate/CLD-based core materials were observed [40]. Furthermore, the operating voltage of several of their modulators actually decreased 20 to 40 % for ^{60}Co gamma-ray irradiation doses as high as 163 krad(Si) at an average dose rate of 2 krad/s. More studies are needed, but preliminary data look promising.

5. CONCLUSIONS

Thermal stability testing and life-cycle stability projections are pointing to 10 years of useful lifetime at continuous operation up to 80 °C for the APC guest-host polymer electro-optic modulator; and, for the new polyimide chemically attached chromophores now under development, it is expected that 10-year lifetimes can be achieved at continuous operation over 100 °C -- and much higher excursions in temperature for short periods of time. With the new highly active chromophores, modulators must be hermetically sealed to exclude ambient air. For more stable operation with the highly active chromophores, light sources that operate at longer wavelengths are recommended (preferably 1550 nm). Operation at high optical power can cause the accumulation of damage due to photo-bleaching the chromophore that will limit the lifetime of the modulator (more noticeable at a wavelength of 1300 nm). The addition of light stabilizer additives should be tested for extending modulator lifetime. In summary, recent technological developments promise more now than ever before that electro-optic polymer modulators will be soon be carving out new applications requiring high bandwidth, low operating voltage, and small flexible devices at low unit cost.

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