

# Effect of Nano-architectural Control on Optical Loss in Electro-optic Polymers

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## ABSTRACT

Nonlinear optical chromophores have been used to obtain guest-host and side-chain polymers. The polymers are fabricated with crosslinking groups attached to both the chromophores and the polymer backbones. The guest-host composites often have micro domains that increase optical loss of the material. When the chromophore is covalently linked to the backbone, the micro domains are avoided and the optical loss of the material is decreased by a factor of 2-3 dB/cm. This nano architectural control is crucial to produce polymer electro-optic devices that are commercially viable.

**Keywords:** electro-optic polymers, optical loss, optical modulators, nonlinear optical chromophores

## 1 ELECTRO-OPTIC POLYMERS

Polymer electro-optic (EO) devices show great promise for high-speed telecom data transmission, broadband radio frequency (RF) signal distribution, and high-speed data transfer within the next generation of microprocessors running at 20 GHz and above (*i.e.*, optical interconnects). EO polymer devices have the potential to increase performance or enable new applications in several industries including telecom networking, wireless communications, and high-performance computing.

One of the critical device performance parameters is the EO activity of the polymer material. Higher EO activity ( $r_{33}$ ) leads to more efficient power performance and smaller device size. Dalton and Robinson have used Monte Carlo simulation methods to predict that  $r_{33}$  can be more than doubled by sterically modifying the shape of the chromophore in EO polymer materials on the nanoscale.<sup>1</sup> This design concept was used to realize high EO activity in poled thin films to achieve an unprecedented  $r_{33}$  of 60 pm/V @ 1300 and reduce the modulator  $V_{\pi}$  to 0.8 V.<sup>2</sup> Recently, Alex Jen's research group at the University of Washington has pushed performance even further by doubling the electro-optic activity of polymers through a process referred to as "nanoarchitectural control."<sup>3</sup> The approach involves grafting a nonlinear optical chromophore onto a polymer backbone to produce nonlinear optical polymers on the scale of about 100 nm. Further synthetic modification of

the material leads to adoption of certain nanoscale geometries that lead to the roughly two-fold increase in electro-optic activity. This work has been a major milestone in EO polymer development, but both the thermal stability and optical loss of the material needs improving to realize commercially viable devices.

## 2 GUEST-HOST EO POLYMER WITH CROSSLINKING GROUPS

It is well known that increasing the temperature at which the EO polymer forms a rubbery state (*i.e.*, the  $T_g$ ) tends to increase the thermal stability of the EO effect. With this in mind, we studied two high  $T_g$  systems to see the effect nanotailoring has on the optical loss performance of EO polymer materials. The first system was a conventional guest-host system where the chromophore (1) is included in the polymer matrix (2) noncovalently (until thermosetting). The chromophore is based on a  $\pi$ -bridge structure that shows increased thermal and photochemical stability over polyene  $\pi$ -bridges.<sup>4</sup> The chromophores made with this bridge show relatively high  $\mu\beta$  while having good processibility. The enhanced photochemical stability is attributed to the presence of alkoxy substituents on the thiophene ring, which prevents hydrogen abstraction and radical formation that may occur when alkyl groups are substituted on the thiophene ring. Guest-host composites of these chromophores can give electro-optic coefficients ( $r_{33}$ ) over 100 pm/V at 1310 nm in APC.<sup>5</sup>

The backbone polymer is a high  $T_g$  polyimide synthesized by grafting a crosslinkable trifluorovinyl ether (TFVE) group<sup>6</sup> on a previously reported hydroxy-functionalized polyimide.<sup>7</sup> The TFVE group has been previously used in crosslinked electro-optic polymers in order to increase chromophore alignment stability.<sup>8</sup> The TFVE group is particularly useful as a crosslinking group in electro-optic polymers because it is fluorinated to reduce optical loss and does not give off condensation products during crosslinking. The crosslinker is also functionalized onto the chromophore to increase compatibility and to incorporate the chromophore into the polymer backbone during thermosetting. It should be noted that attaching the TFVE group to the acceptor increasing the  $\mu\beta$  of the chromophore since the TFVE group itself is electron withdrawing and has a dipole moment.

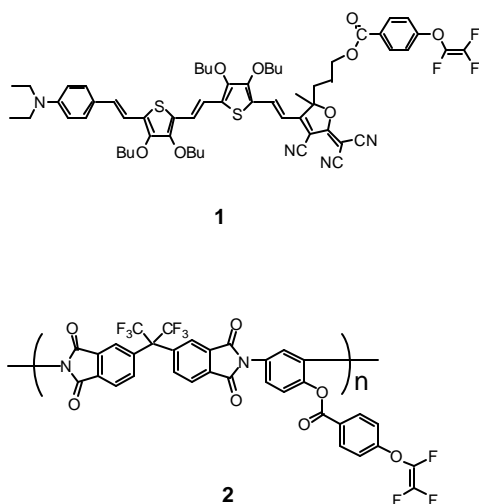


Figure 1: Chemical structures of the polymer (1) and the chromophore (2) for guest-host composites.

Optical quality thin-films of the guest-host composite were spin deposited on 4-inch diameter silicon wafers. The chromophore (1) loading was approximately 20% by weight in the polymer matrix (2). The thickness of the film was approximately 3  $\mu\text{m}$ . The films were soft baked at elevated temperatures (80–100  $^{\circ}\text{C}$ ) under vacuum for several hours to remove residual spinning solvent. Optical loss measurements were carried out using a prism coupling technique. The average optical loss of five different areas in the thin film was 3.88 dB/cm. This optical loss is relatively high EO polymers materials, and is most likely the results of some degree of phase separation. Phase separation in a fluorinated guest-host composite leads to micro-domains that scatter the light at telecom wavelengths (1.31 and 1.55  $\mu\text{m}$ ). A scanning electron micrograph (SEM) of the cross section on of the guest-host composites shows the micro domain formation caused by the phase separation. The globular particles are attributed to aggregates of the chromophore.

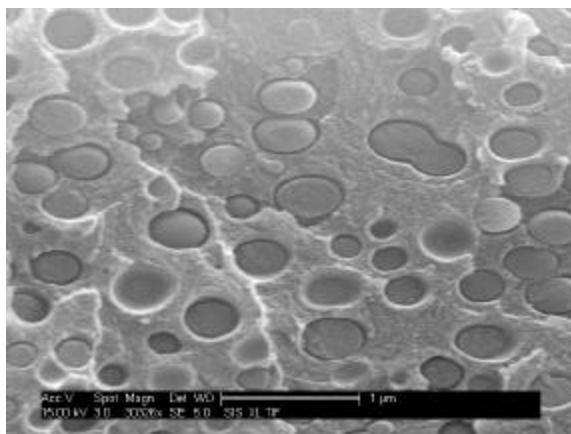


Figure 2: SEM of guest-host composite

### 3 SIDE-CHAIN EO POLYMER WITH CROSSLINKING GROUPS

The second system was a side-chain polymer (3), shown in Figure 3, where the chromophore is covalently attached to the polymer to produce a nonlinear optically active nanostructure. The backbone (4) of the polymer used for side-chain attachment and the crosslinking groups were the same as those used in the guest-host composite. The same backbone and crosslinking groups were chosen to obviate any problems associated with structure dependent morphology differences. For the side-chain polymer, a chromophore having a crosslinkable group on the acceptor was grafted onto the polymer backbone followed by the crosslinker. This methodology allows the adjustment of the crosslinker/chromophore ratio to optimize the loading density and processibility of the resulting NLO polymer. After the reaction to form the polymer, unreacted chromophore is removed by repeated precipitation of the polymer. The loading density of the chromophore in the polymer can be determined by monitoring the optical absorption of the chromophore. The refractive index also scales with the amount of chromophore (Figure 4), which is potentially useful as a tunable refractive index system for waveguide fabrication.

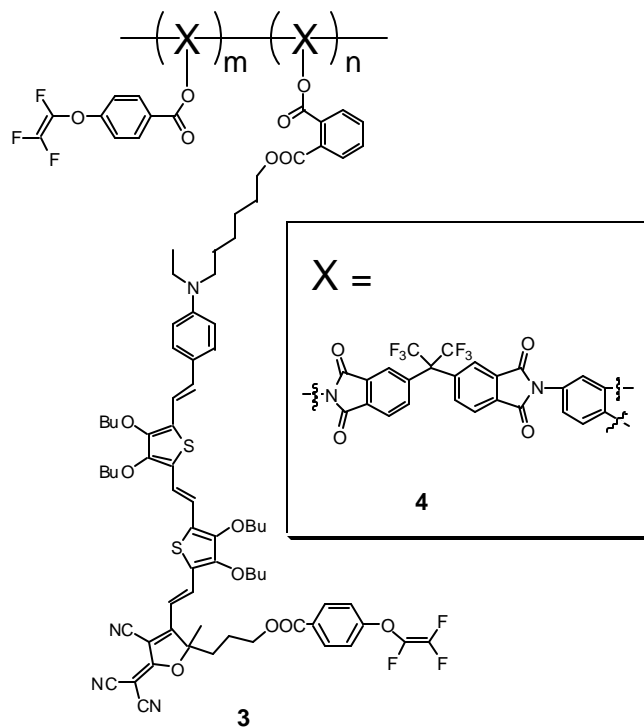


Figure 3: Side-chain polymer (3) and the side-chain polymer backbone (4)

## 4 CONCLUSIONS

Optical loss in electro-optic polymers has been reduced by incorporating chromophores as side-chains in high  $T_g$  polyimides. The reduction in optical loss is facilitated by the chromophore's incorporation into the nanostructure of the polymer backbone, which avoids micro domain formation. The optical loss of the material approaches what is necessary to produce a commercially viable electro-optic polymer modulator with a total optical loss (material loss plus fiber coupling loss) of 6 dB. Further studies are being aimed at reducing material loss further by increasing fluorination of the chromophore and polymer backbone as well as decreasing device length.

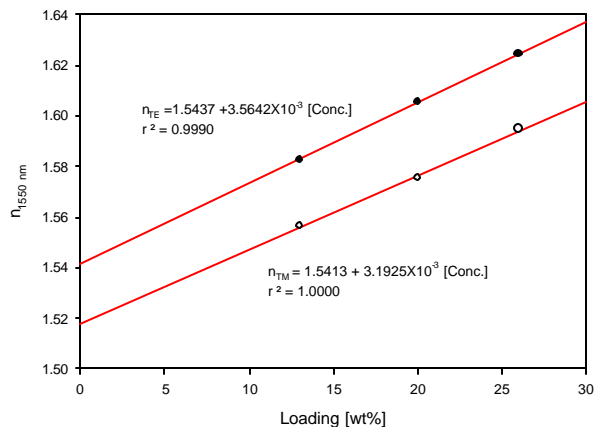


Figure 4: Refractive index vs. chromophore loading in a side-chain polymer.

## REFERENCES

Optical quality thin films of the side-chain polymer were spin deposited on 4inch diameter silicon wafers. The films were heated at (80-100 °C) under vacuum for the same amount of time as the guest-host composites. The thickness of the films was approximately 3  $\mu\text{m}$ . Optical loss measurements were performed by prism coupling. The average optical loss for five areas of the thin film was 1.9 dB/cm, which is a factor of two improvement over the guest-host system presented here. SEM images of a cross section of the thin film showed no micro domain phase separation in the side-chain polymer, which validates that the chromophore has been included in the nanostructure of the polymer. The nanostructure of the current side-chain polymers is on the order of 100 nm, which is well below the size that may cause significant scattering of  $\mu\text{m}$ -wavelength light. This reduction in optical loss is significant especially if one considers the propagation length of a typical Mach-Zehnder modulator. If the propagation length is 3 cm, then a device fabricated from the guest-host system would have a fundamental material loss of around 12 dB, which is more than *twice* that of the 6 dB *total* optical loss (*i.e.*, material loss plus fiber coupling loss) in typical commercial optical modulators made from inorganic material. On the other hand, modulators made from the side-chain materials would have a fundamental material loss of 6 dB, which is near the range of commercially available modulators if < 1 dB/face coupling loss can be achieved.<sup>9</sup> To reduce the total loss of the device, one can either decrease the total device length or decrease the material loss. Further reduction in material optical loss can be expected by increasing the fluorine content of the chromophore and polymer backbone.

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- <sup>9</sup> Less than 1 dB of coupling loss in polymer modulators has been reported, for example see: Kim, S. K. *et al.*, *J. Kor. Phys. Soc.* **2003**, *43*, L645.