

Electro-optic polymers for high speed modulators

M. Balkrishnan, M. B. J. Diemeer, A. Driessen,

Integrated Optical Microsystems, MESA⁺ Institute for Nanotechnology, P.O. Box 217, 7500 AE Enschede, The Netherlands.

M. Faccini, W. Verboom, D. N. Reinhoudt

Laboratory of Supramolecular Chemistry and Technology, MESA⁺ Institute for Nanotechnology, P.O. Box 217, 7500 AE Enschede, The Netherlands.

A. Leinse

LioniX BV, P.O. Box 456, 7500 AH Enschede, The Netherlands.

Abstract: Different electro-optic polymer systems are analyzed with respect to their electro-optic activity, glass transition temperature (T_g) and photodefinable properties. The polymers tested are polysulfone (PS) and polycarbonate (PC). The electro-optic chromophore, tricyanovinylidenediphenylaminobenzene (TCVDPA), which was reported to have a highest photochemical stability [1] has been employed in the current work. Modified TCVDPA with bulky side groups has been synthesized, and a doubling of the electro-optic coefficient (r_{33}) compared to the unmodified TCVDPA has been shown. The plasticizing effect of the chromophore, has been reduced by attaching it to the polymer backbone. SU8 (passive) and PC-TCVDPA (active) channel waveguides were fabricated by photodefinition technique and the passive waveguide losses were measured to be 5 dB/cm at 1550 nm.

Over the past few years there has been an increased interest in electro-optic polymers for telecommunication applications. Due to their potential for low drive voltage, integration ability, low optical losses in the 1.3 and 1.55 μm telecommunication windows, and low dispersion of refractive index between optical frequencies and millimeter waves, electro-optic polymer modulators are being targeted for > 40 Gb/s data rate communication systems. Polymer electro-optic modulators operating at 1.3 μm with drive voltages < 1 V and modulation bandwidths ranging from 150-200 GHz have been demonstrated [2]. Practical integration of these devices to telecommunication systems depends not just on the modulation and bandwidth milestones, but also on short and long term performance requirements.

Polymer electro-optic modulators typically consist of waveguides with polymer core material and cladding layers, designed to form either a Mach-Zehnder interferometer, or a microring resonator. In both cases the core material consists of electro-optic chromophores either doped into, or covalently attached to the host material. The chromophores are responsible for the electro-optic activity in the material. The specific chromophore used will determine the photochemical stability of the device. The host material plays a critical role in the overall design, fabrication methods, and thermal stability. The chromophore and the host material together determine the optical losses. The chromophore can be simply doped in the host (guest-host polymer), attached as side chain, or even crosslinked between different polymer backbones.

To date several host materials like PMMA, polyimide, polyurethane etc., have been used for both material and device studies. In the current work we report the usage of the TCVDPA chromophore in two different host materials namely, polysulfone and polycarbonate (the high T_g version). Solutions of PS and PC were prepared in

cyclopentanone. The solutions were filtered through a 0.2 μm acrodisc filter, spin coated on ITO coated glass wafers, and dried in a vacuum oven at 95° C for 8 hours. The samples were then poled by heating them close to their T_g and applying an electric field in the order of 100 V/ μm for 20 minutes. Non linear optical properties were evaluated by measuring the r_{33} coefficient by the Teng Man reflection technique at 830 nm [3].

PS-TCVDPA constitutes the guest-host system in which TCVDPA chromophore is simply dissolved in the PS host. Films with different concentrations of TCVDPA in PS were prepared and the r_{33} coefficient was measured. Figure 1 shows the plot of r_{33} versus chromophore concentration expressed in wt%.

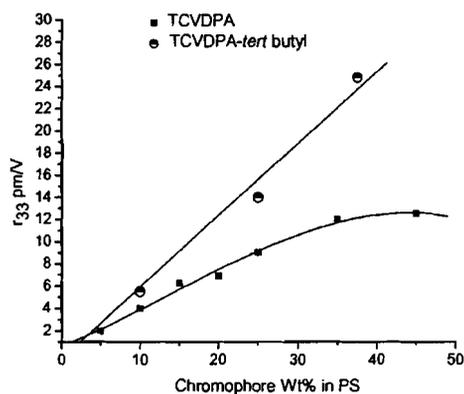


Figure 1

Figure 1: Variation of r_{33} with TCVDPA and TCVDPA-*tert* butyl concentrations in PS. The concentrations of TCVDPA with *tert*-butyl groups is expressed as effective concentration of TCVDPA for comparison

Figure 2: TCVDPA (2a) and TCVDPA with *tert*-butyl side groups (2b)

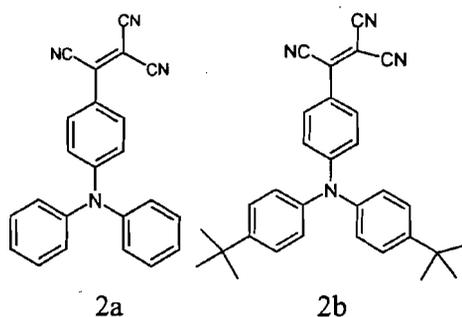


Figure 2

From figure 1 it can be seen that the r_{33} increases linearly up to a concentration of about 15 wt%, above which the curve starts to flatten. The maximum r_{33} measured was 12.5 pm/V. The flattening can be explained by increased intermolecular dipole-dipole interaction between the chromophores causing antiparallel clustering with no contribution to the electro-optic effect. The intermolecular interaction between the chromophores can be reduced by attaching bulky side groups to the chromophores, making them more spherical and thereby preventing their closer approach [4]. This has been demonstrated by testing TCVDPA modified with *tert*-butyl bulky side groups. TCVDPA and TCVDPA with *tert*-butyl side groups are shown in figure 2. In figure 1 the r_{33} of the TCVDPA chromophore modified with *tert*-butyl side group is also shown. A linear increase in r_{33} was found upto 40 wt% of the chromophore, without any interaction. TCVDPA with the *tert*-butyl side group gave the best result with an r_{33} of 25 pm/V, a doubling effect compared with TCVDPA without side group. One of the advantages of using polysulfone as host is its high T_g of about 190°C. Chromophores act as plasticizers and reduce the T_g of the host polymer drastically when added as guest. Figure 3 shows this effect. The T_g of polymers with different concentrations of the chromophores was determined by observing the buckling of the gold layer of 100 nm thickness sputtered onto a polymer layer on a silicon wafer, as the temperature of

the polymer is slowly ramped. Figure 3 shows the T_g as a function of the chromophore concentration for the two chromophores. From the figure 3 it can also be seen that the chromophore with a lower molecular mass has a higher plasticizing effect. This sets a limit to the maximum achievable chromophore concentration so that the T_g is not considerably reduced.

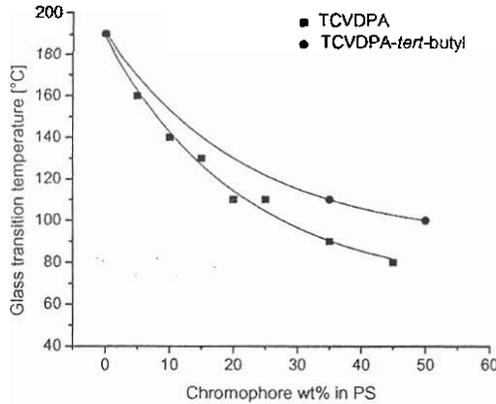


Figure 3: Variation of T_g with chromophore concentration in PS

The plasticizing effect can be overcome by attaching the chromophore to the polymer backbone. This was demonstrated in the PC-TCVDPA system. By this technique 50 wt% of TCVDPA was incorporated in PC without any reduction of T_g (T_g of undoped PC is 190° C). The T_g was even raised to 225° C with chromophore addition. PC-TCVDPA was spun as thin film and the r_{33} value was found to be 14 pm/V. Poling was done at 225° C for 30 minutes with a field strength of 100 V/ μ m. When the chromophore is attached to the polymer backbone, the poling efficiency is slightly reduced. But this is offset by the reduced intermolecular interaction due to the restricted motion of the chromophores and hence a slight increase in the r_{33} value is seen compared with PS-TCVDPA. When PC is equipped with TCVDPA with *tert*-butyl groups, it is expected that the intermolecular interactions will be further reduced. A 2 μ m film of PC-TCVDPA was spun on a Si wafer, dried in a vacuum oven for 8 hours and a refractive index of 1.62 was measured at 1550 nm using a Woolam ellipsometer.

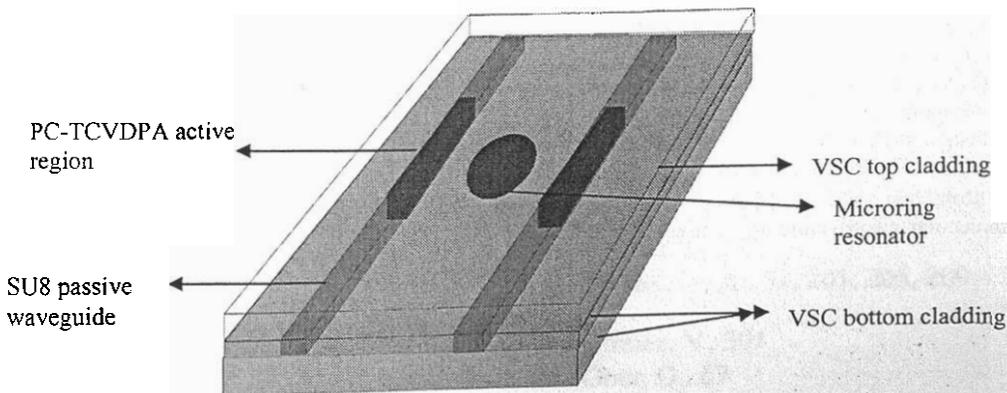


Figure 4: Schematic of a Inverted ridge defined in VSC with passive SU8 waveguide and active PC - TCVDPA region

Waveguides were fabricated by a combination of reactive ion etching and photodefinition (figure 4). Firstly, inverted ridges were photodefined in a cladding material (VSC) with a refractive index of 1.5. The photodefined channels were then filled with SU8 as passive waveguide material. Losses in the SU8 waveguides were determined by cutback technique to be 5 dB/cm. This passive waveguide will be partially removed by photodefinition and replaced with PC-TCVDPA by spin coating, as active material for device fabrication. A SEM picture of a photodefined inverted ridge with PC-TCVDPA on top is shown in figure 5. The refractive index of SU8 is 1.58 at 1550 nm and hence losses because of mode mismatch at the active / passive interface is expected to be negligible. The residual slab heights of the active and passive layers will be etched back to zero by reactive ion etching.

In conclusion, TCVDPA and its modification were incorporated in PS and PC. TCVDPA with *tert*-butyl as side groups was found to be effective in reducing the intermolecular interactions and thereby yielding the highest measured r_{33} of 25 pm/V. The reduction of T_g by chromophore addition was completely prevented by attaching it to the polymer backbone. Ridge waveguides were fabricated by photodefinition and the losses were measured to be 5 dB/cm in the SU8 passive waveguides.

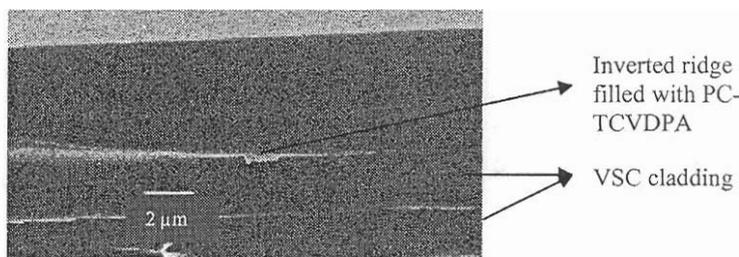


Figure 5: SEM picture of a photodefined ridge in VSC with PC-TCVDPA layer above

This research work is supported by the Dutch Technology Foundation STW, Applied Science Division of NWO and the Technology Program of the Ministry of Economic Affairs and carried out within the framework of the project TOE 6067 "Broadband and wavelength selective modulators for optical communication based on electro-optic polymers"

References:

- [1] A. G. Gonzalez, G. I. Stegeman, A. K. Y. Jen, X. Wu, M. Canva, A. C. Kowalczyk, X. Q. Zhang, and H. Z. Lackritz, "Photostability of electro-optic polymers possessing chromophores with efficient amino donors and cyano containing acceptors", *J. Opt. Soc. Am, B* vol 18, pp 1846-1848, 2001.
- [2] L. R. Dalton, A. Harper, A. Ren, F. Wang, G. Todorova, J. Chen, C. Zhang and M. Lee, "Polymeric Electro-optic modulators", *Ind. Eng. Chem. Res.* vol 38, pp 8-33, 1999.
- [3] C. C. Teng and H. T. Man, "Simple reflection technique for the measuring the electro-optic coefficient of poled polymers", *Appl. Phys. Lett.*, Vol 56, pp. 1734-1736, 1990.
- [4] B. H. Robinson and L. R. Dalton, "Monte carlo statistical mechanical simulations of the competition of Intermolecular electrostatic and poling field interactions", *J. Phys. Chem A*, vol 104, pp 4785-4795, 2000.