POLING OF EO POLYMERS - CORONA DISCHARGE PROCESS OPTIMIZATION

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Introduction

Nonlinear optically (NLO) active polymers are promising substitutes of NLO active inorganic materials in modern electronics. NLO activity of polymers can be obtained by electric field poling where NLO coefficient can be described as:

$$d_{33} \sim \mu\beta NE / kT$$

where μ – is the dipole moment of chromophore, β – first molecular hyperpolarizability, N – chromophore number density. For polymer poling purposes the corona triode device seems very attractive due to the fact that one can have good estimation of poling field, low probability of electrical breakdown in the sample, etc. We have built a computer controlled corona triode device which allows us to capture current-voltage characteristics of the system as well as perform EO polymer poling at constant grid potential or sample current.

Method

The poling field is created in a positive corona discharge process when the ions accumulate on the surface of the sample. Ion flow and therefore the surface charge of the sample is controlled by the altering voltage on the grid that is located between the sample and corona wire as can bee seen in Figure 1. Following parameter impact on NLO efficiency has been investigated:
1) Grid to sample distance - can be varied by choosing different grid spacers.
2) Needle to grid distance – adjustable with a screw
3) Spacer type
4) Surrounding atmosphere composition
5) Grid voltage
After poling the sample NLO efficiency is determined by second harmonic generation (SHG) measurements using Maker fringe technique.

Results

• Optimal grid to sample distance found to be 6 mm (Fig. 2)
• Best results obtained using a grid spacer with conical hole. In this case the spacer works as a "ion lens" concentrating the ions to the middle of the sample.
• When varying corona needle to grid distance we found that gas discharge can take place. In this case avalanche type ion flow increases the sample charge and therefore the poling voltage. Thus one can have higher NLO coefficients (see Fig. 3).
• The surrounding atmosphere is also relevant. In air during corona discharge ozone is generated. Ozone degrades the NLO active chromophores which can be seen as material bleaching, e.g., for IPB in PMMA matrix (Fig. 4). This is can be prevented if the nitrogen flow is applied.
• From I-U characteristics (Fig. 5) we see that sample current to grid voltage dependence is Ohmic in case when corona and grid voltage difference is kept constant. However a threshold grid voltage must be applied for poling to take place. This is due to the fact that under threshold grid voltage the ions lack energy to reach the sample.
• The second harmonic (SH) scan for samples poled at different grid voltages shown in Fig. 6. We noticed that at certain grid voltages in the center of the sample the NLO efficiency decreases dramatically (see also Fig. 5). This can be caused by increased amount of charge concentration in the centre of the sample which enforces oriented dipole movement or mass transport. Further investigation showed that light scattering takes place in the oriented part of the sample at 532 nm and 632.8 nm, however not for 1064 nm (Fig. 7).
• From the surface images (Fig. 8) made by (a) optical, (b) SH microscopes and (c) SEM surface irregularities are noticed which cause the light scattering and in the same time are NLO active. Moreover, in the poled region spatial changes take place. SH spatial measurements show formation of spatial irregularities with increased oriented chromophore content (Fig. 9).

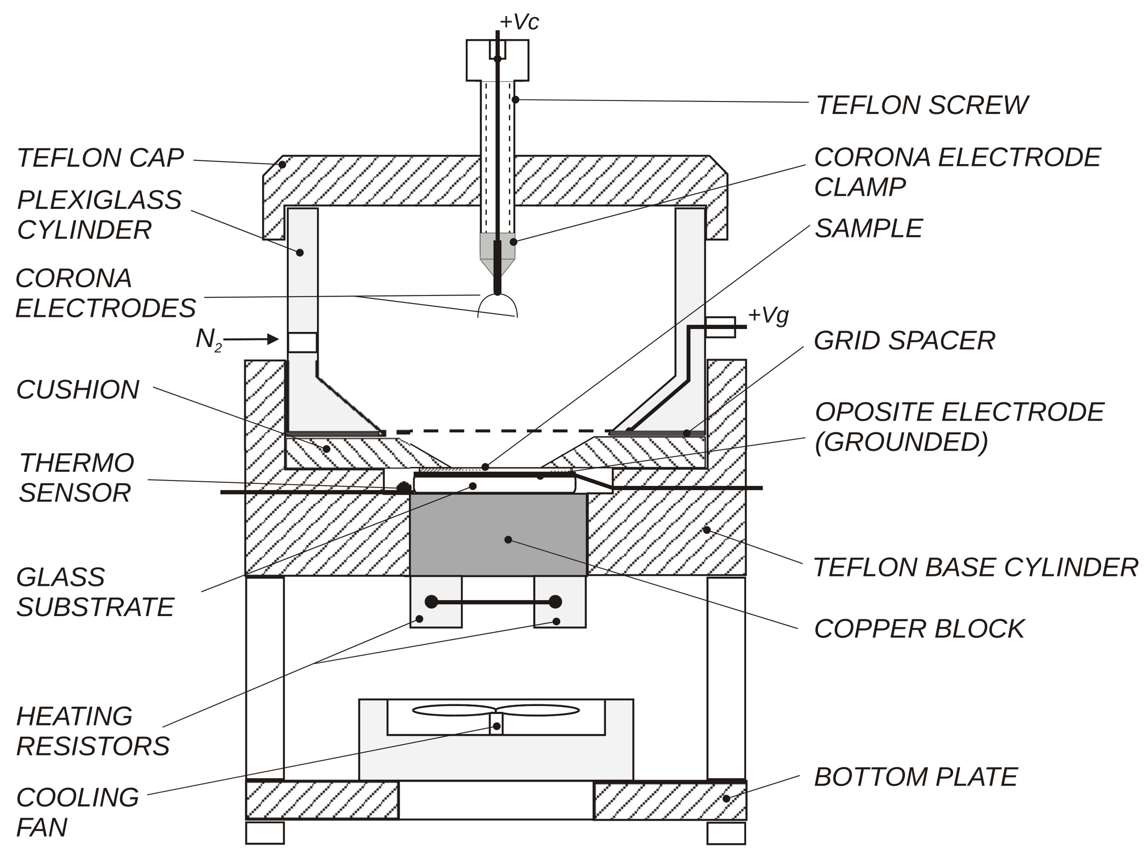

***Figure 1** The principal scheme of corona discharge device*

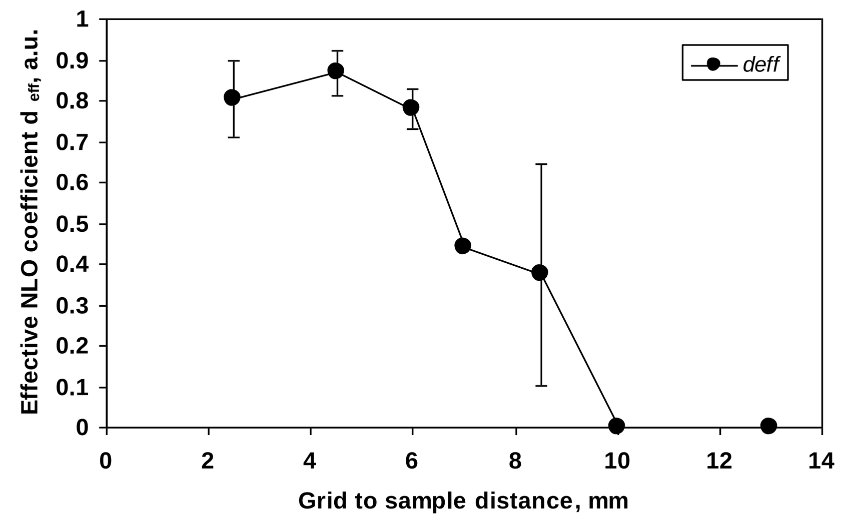

***Figure 2** Effective NLO coefficient as a function of grid to sample distance*

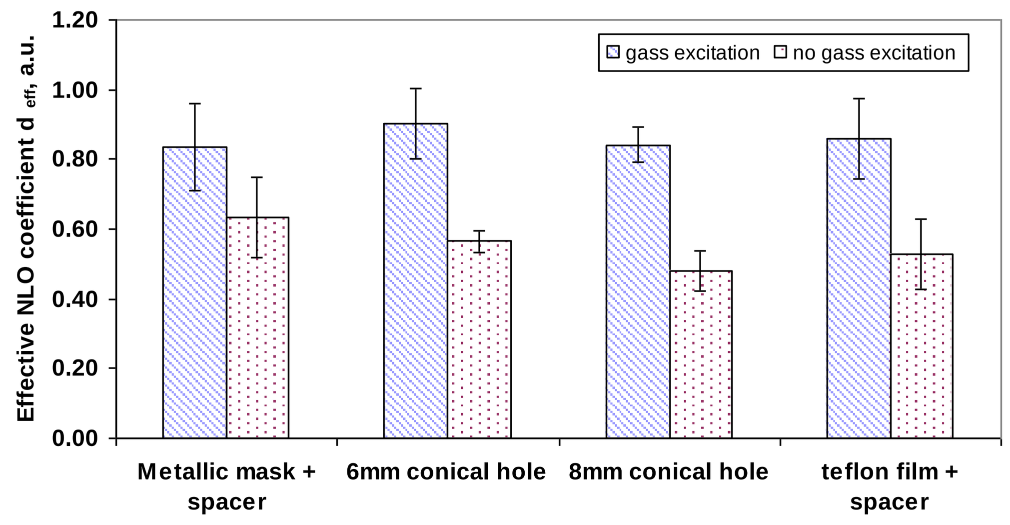

***Figure 3** Effective NLO coefficient with different spacer forms and gas excitation effect*

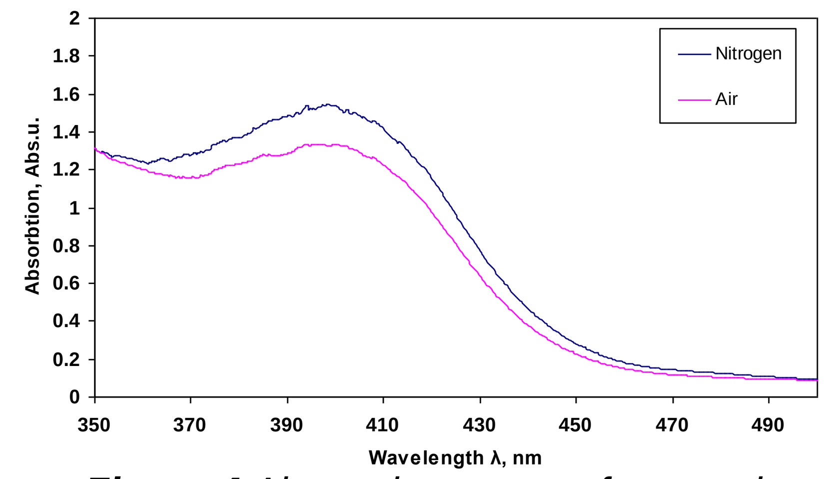

***Figure 4** Absorption spectra for samples poled in air and nitrogen atmosphere*

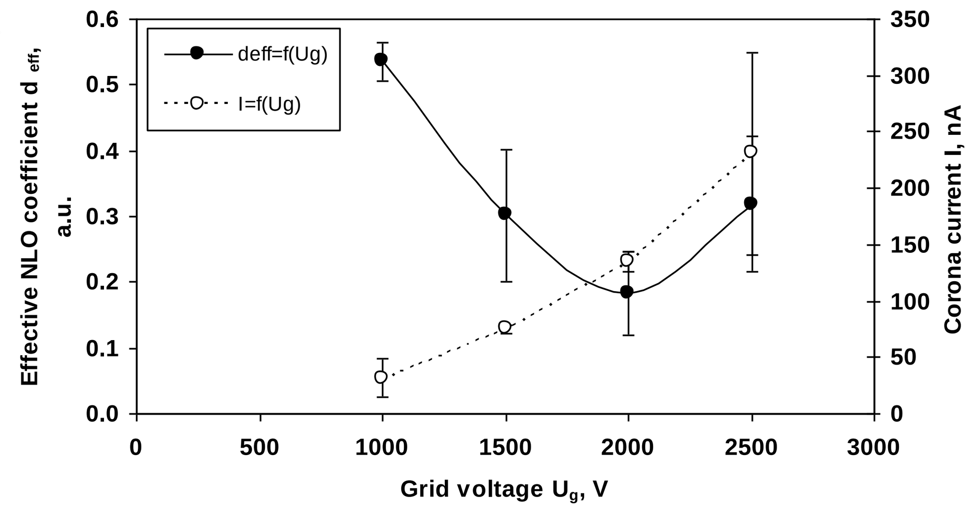

***Figure 5** Effective NLO coefficient and corona current as a function of grid voltage*

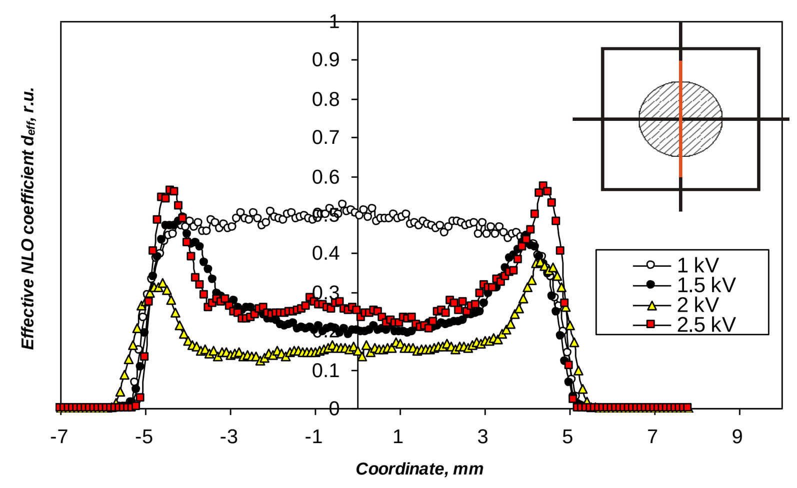

***Figure 6** SH scan of samples poled at grid voltage 1 kV and 1.5 kV*

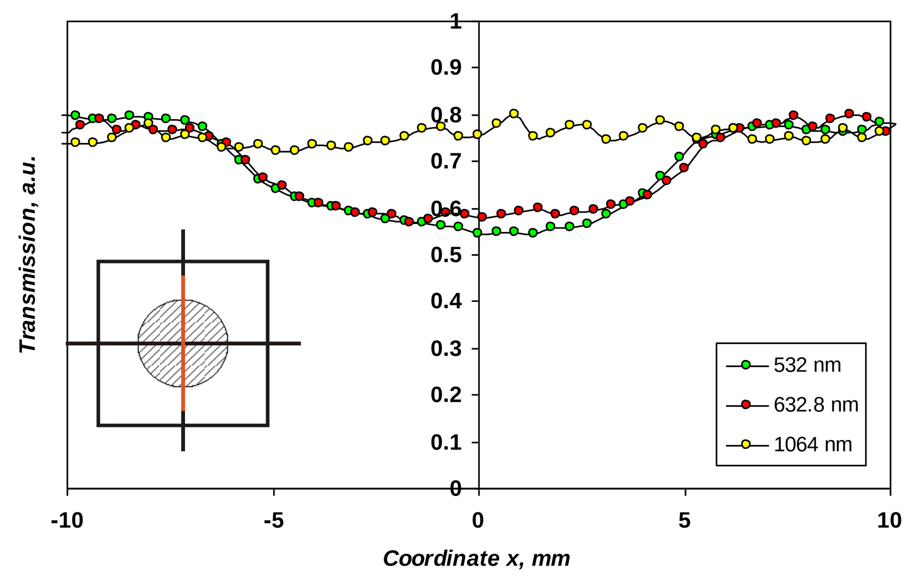

***Figure 7** Transmission at 532, 632.8 and 1064 nm of sample poled at grid voltage 1.5 kV*

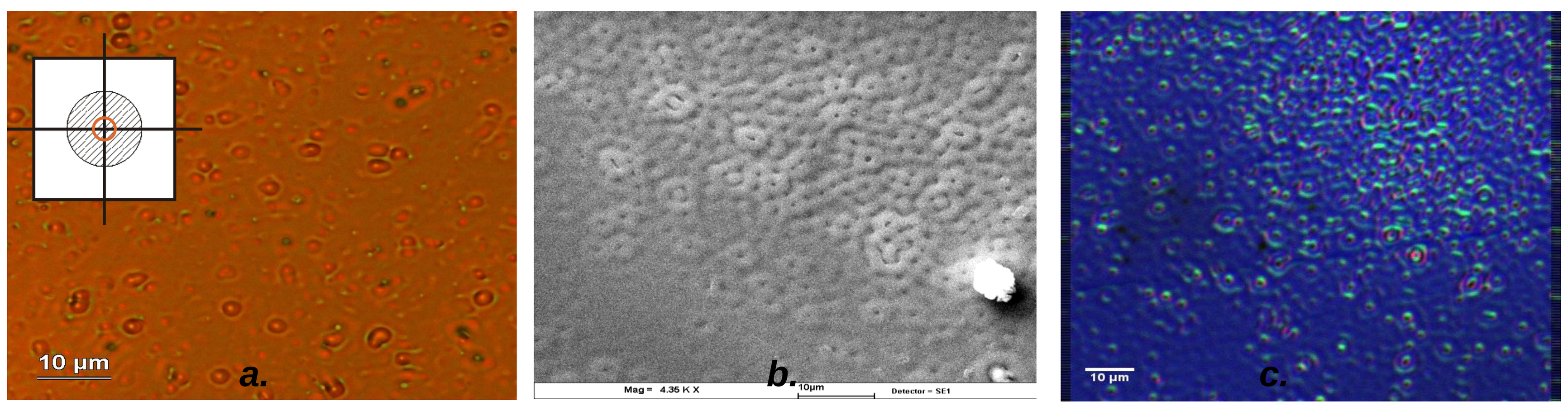

***Figure 8** Images made using (a) optical microscope, (b) SEM and (c) second harmonic microscope*

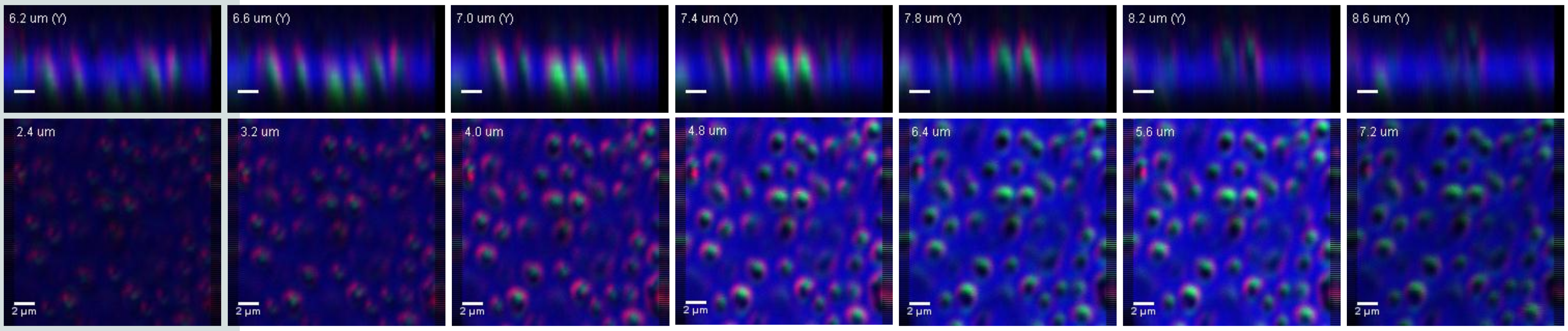

***Figure 9** Second harmonic spatial images: XZ plane – first row, XY plane – second row*

Conclusions

•Surface and spatial changes are noticed in the region where both elevated temperature and certain electric field is applied. These conditions cause formation of surface and spatial irregularities that are NLO active. However, as their size is close to optical wavelength light scattering takes place which reduces overall effective NLO activity of material. Thus one must choose optimal conditions for both orientation order and homogeneity.
• Corona discharge optimization is a difficult process involving many variable parameters. Further poling procedure investigations are necessary to be able to improve poling reproducibility.

Acknowledgements

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