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Effect of Corona Poling and Thermo Cycling Sequence on NLO Properties of The Guest-Host System

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In the case of doped polymer system SHG efficiency is proportional to the concentration and orientation degree of NLO-active molecules. Unfortunately, corona poling realised at elevated temperatures causes concentration decrease of NLO-active molecules due to crystallization. On the basis of our studies of the film optical images, refractive index and SHG measurements of the dimethylamino-benzylidene 1,3-indandione and PMMA guest-host system, we have demonstrated that optical quality is improved and second order NLO efficiency is higher, when the external poling electric field is switched on from the very beginning of the sample heating process.

Keywords: corona poling; crystallite formation; NLO polymer; polar molecules

INTRODUCTION

In the last decade, low-cost organic nonlinear optical polymers with extra large non-resonant nonlinear optical coefficients, fast response, and a low dielectric constant have been put forth as promising candidates for future non-linear optical (NLO) applications such as frequency doublers, optical storage devices, electro-optic switches, and modulators [1–3]. A polymer with incorporated active nonlinear organic molecules is one group of such materials. However, since molecules in the polymer matrix are oriented randomly it is essential to impose polar orientation to break down the centro-symmetric ordering and to obtain the second order nonlinear optical effect. A strong external electric field, like corona discharge, is employed for orientation of polar molecules [4]. In most cases polarization by corona discharge is thermo-assisted. The usual poling procedure is to heat the guest-host polymer film close to the glass transition temperature and then apply

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the chromophore orienting external electric field [5–8]. According to our observations the timing of poling field can affect significantly the optical quality and NLO efficiency of the film. In this study we show the importance of poling field timing on the dimethylaminobenzylidene 1,3-indandione (DMABI) and PMMA guest-host system NLO properties.

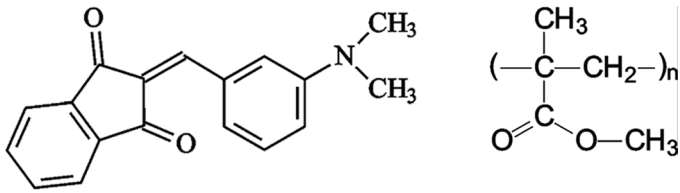
EXPERIMENTAL

Sample Preparation

An appropriate mixture by weight of at Riga Technical university synthesized polar organic molecules DMABI and PMMA (*Aldrich*, catalogue no. 445746), the structures of both are shown in Scheme 1, are dissolved in chloroform. The total concentration 50 mg/ml of both ingredients was used to produce a guest-host polymer system. The films with concentrations of 3, 5, 10, 15, and 20 wt% were spin-coated (speed – 500 rpm, acceleration – 100 rpm/s, spinning time – 40 sec.) on indium tin oxide covered glass substrates. After spin-coating the samples were dried at ambient temperature ($\sim$25°C) for 2 days to remove the chloroform. The obtained polymer films were 1 to 2 μm thick.

Corona Poling Procedure

To produce non-centro-symmetrical media the DMABI (ground state dipole moment 3.74D [9]) molecules in the samples were oriented by high-voltage electric field corona poling. Corona voltage of 6–8 kV was applied to a tungsten wire (diameter 25 μm) at the distance of 1 cm from the sample surface. During the poling procedure corona current density was held constant at 1 μA/cm^2. The samples were corona poled through a mask with diameter of 0.8 cm and cooled to



(a) (b)

SCHEME 1 Chemical structure of the DMABI molecule (a) and the polymer (methyl methacrylate) matrix (PMMA) (b).

TABLE 1 Corona Poling Procedures

Type	Parameter	Heating	Annealing	Poling	Cooling
1.	Temperature	RT → 120°C	→	120 °C	120°C → RT
	I_{Corona}	0.5 μA		0.5 μA	0.5 μA
	Step Time	(∼25 min)		10 min	(∼30 min)
2.	Temperature	RT → 120°C	→	120°C	120°C → RT
	I_{Corona}	0 μA		0.5 μA	0.5 μA
	Step Time	(∼25 min)		10 min	(∼30 min)
3.	Temperature	RT → 120°C	120°C	120°C	120°C → RT
	I_{Corona}	0 μA	0 μA	0.5 μA	0.5 μA
	Step Time	(∼25 min)	60 min	10 min	(∼30 min)

Current intensity values should be below temperature values.

room temperature under applied electric field maintaining a constant current [8]. We have tested the impact of three different poling procedures (see Table 1) on the NLO efficiency and optical quality of the film. The first is our suggested procedure, the second and especially the third are the widely used ones [5–8].

To avoid EFISHG signal from charges trapped on the film surface the non-linear coefficients d_{33}, d_{31}, were measured usually 2 days after poling.

Optical Images

Optical images were obtained by a "Nikon Eclipse L150" high resolution digital optical microscope. The images of the samples were taken twice. The first time – two days after sample preparation and the second time – one day after the orientation process.

Determination of the Nonlinear Optical Coefficients d_{ij}

The experimental set-up for second harmonic generation, employing a Q-switched Nd: YAG laser operating at 1064 nm wavelength with repetition rate of 2000 Hz, average power 200 mW, pulse duration 250 ns and beam diameter ∼1 mm, is described elsewhere [9]. The second harmonic intensities were recorded as functions of the incidence angle and polarization (Maker fringe technique). The $C_{\infty v}$ symmetry was assumed for corona poled films characterized by three nonzero NLO coefficients – d_{33}, d_{31} and d_{15}. As it's done usually for poled polymer films [10], according to Kleinman symmetry, we assume that $d_{31} = d_{15}$. The M-line method was used to measure film thickness and refractive indices at 532 nm and 1064 nm. The NLO coefficients were obtained by least square fit of the experimental

curves to theoretical approximation. The theoretical value of second harmonic intensity (SHI was calculated using Herman–Hayden [10] approach, taking into account absorption of the film. The fitting was carried out in two steps: the value of d_{31} was evaluated from experimental *s-p* polarized SHI, then the d_{33} was calculated from the *p-p* SHI. The x–cut quartz crystal was used as reference ($d_{11} = 0.3$ pm/V [11]).

RESULTS AND DISCUSSION

In the case of doped polymer system SHG efficiency is proportional to the concentration and orientation degree of the NLO-active molecules [12]. Unfortunately, poling realized at elevated temperature causes the concentration decrease of NLO-active molecule due to crystallization, as it was also observed recently by Rau *et al.* [13,14]. To estimate impact of different orientation procedures on the crystallite formation we have compared optical images of polymer films before and after poling. First of all, we would like to draw attention on investigations of 10 wt% DMABI/PMMA samples by the reason that in previous experiments this concentration is within a range of the highest NLO efficiency [9]. For this concentration, in the freshly prepared samples, we have observed $\sim$4000 small crystallites per mm^2 (see Fig. 1). Poling through a mask allowed us to compare amount of crystals in poled and non poled areas on the same sample exposed to the same heat treatment. In areas that have not been exposed to the electric

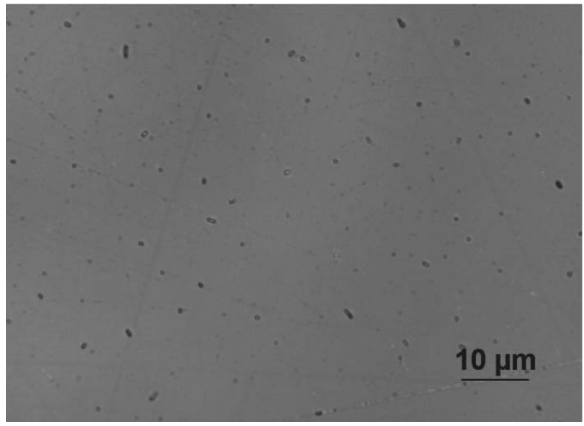


FIGURE 1 High resolution images of the 10 wt% DMABI/PMMA before orientation.

field (see Fig. 2b, 2d, 2f) for all the types of orientation processes (see Table 1.) the number density of crystallites is very high (>50000 cryst./mm^2). In case of the film area affected by the electric

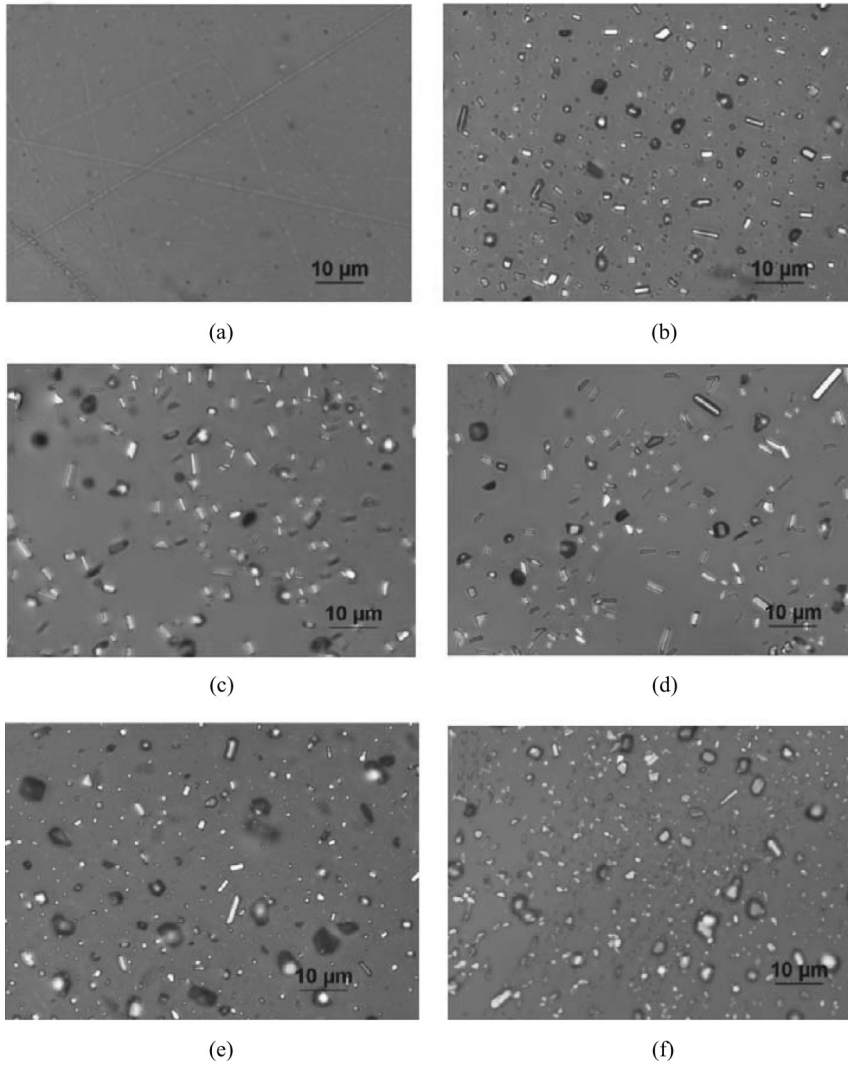


FIGURE 2 High resolution images of 10 wt% DMABI/PMMA after corona poling a) first type orientation takes place, b) first type orientation doesn't take place, c) second type orientation takes place, d) second type orientation doesn't takes place, e) third type orientation takes place, f) third type orientation doesn't take place.

field one could find essentially different picture. Number density ($\sim$5000 cryst./mm^2) and size of crystallites (see Fig. 2*a*) after the first type of orientation procedure stay approximately the same as for freshly prepared sample. As one can see from Figure 2*c* and Figure 2*e*, the additional amount of crystallites are present in the film once the second ($\sim$ 35000 cryst./mm^2) or third ($\sim$ 52000 cryst./mm^2) type of poling procedures was used. Crystallite number density increases with the time of the sample being exposed to elevated temperature. One of the possibilities to reduce the crystallite formation is to minimize this period. Unfortunately, the most critical stage is heating from RT to orientation temperature, when significant crystallization takes place. According to our observations, one could compare Figure 2a with 2c, switching on corona discharge during this heating stage allows us to suppress crystallite formation.

From the optical images we could obtain only a number density of crystallites, but in general we are interested to achieve high NLO efficiency after poling, which is proportional to the number of active molecules per volume. We have estimated the actual active molecule concentration (see Table 2) of DMABI dissolved in polymer matrix by measuring refractive index at 532 nm, what should be linear proportional to a concentration in range 0–15 wt%. If one analyses NLO efficiency (in our case we use d_{33} values, see Table 2) of the samples poled by procedures 1, 2 and 3, it is not sufficient to take into account active molecule concentrations to explain differences obtained from the SHG measurements. For example: NLO efficiency of the sample oriented by first type of poling procedure is 1.66 times larger in comparison with sample after second type of poling procedure. At the same time actual chromophore concentration ratio in PMMA matrix is just 1.25 times larger. One of the causes of this disagreement could be light scattering by the crystals, what decreases NLO efficiency. Reduced crystal grows yielded in higher active chromophore concentration in volume and less light scattering loses. Both effects are increasing NLO efficiency of the bulk material.

TABLE 2 Actual Concentration and Optical Properties of Poled 10 wt% DMABI/PMMA Films

Orientation type	Refractive index	Actual concentration (wt%)	d_{33} (pm/V)
1	1,5804 $\pm$ 0,0011	$\sim$7,5	5.5 $\pm$ 0,2
2	1,5669 $\pm$ 0,0021	$\sim$6	3.3 $\pm$ 0,15
3	1,5394 $\pm$ 0,0017	$\sim$4	1.4 $\pm$ 0,07

In Figure 3 we have plotted the NLO efficiency enhancement by the first poling procedure, in comparison to the second one as function of the initial chromophore concentration in PMMA matrix. To give some explanation of the external electric field influence on aggregate formation at different concentrations we have to take into account the polar molecule electrostatic interactions. During orientation there are two electrostatic forces acting on polar chromophore molecules: first is the intermolecular dipole – dipole and second is the external electric field – dipole one. Dipole – dipole interaction tends to orient dipoles antiparallel, but external electric poling field – parallel. Antiparallel dipoles attract each other and could accelerate aggregation, but parallel dipoles exhibit repulsion what could prevent aggregation. The probability of aggregate formation is small at low concentrations due to large distance between molecules (small attraction force) and external electric field only orients the dipoles. In films with high chromophore concentrations the dipole – dipole interaction is dominating and the external electric field practically can not influence formation of aggregates. In between these two extremes there should be a concentration range at which the external electric field – dipole interaction energy is comparable with dipole – dipole energy and could affect crystallite formations. In the case of DMABI/PMMA (see Fig. 3) the maximum difference of SHG efficiency between first and second type of orientation process was observed at concentration of $\sim$10 wt%. The highest SHG efficiency in DMABI/PMMA is known to be within the 10–15 wt % range of concentrations [9]. It means that by choosing the appropriate (first) type of orientation procedure one could significantly increase the NLO efficiency of DMABI/PMMA guest-host films.

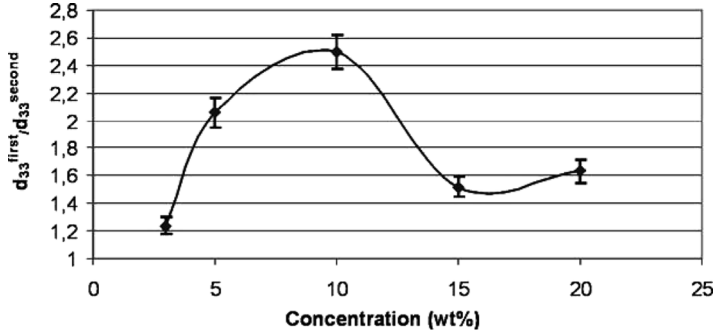


FIGURE 3 Ratio of SHG efficiencies for samples oriented by the first and the second type procedures described in text.

CONCLUSION

The NLO efficiency of the investigated guest-host films are strongly affected by crystallite grows during corona poling procedure at elevated temperatures. Number density of crystallites is increasing with time of the sample being exposed to elevated temperature. Presence of external electric field is preventing this, unwanted, crystallization. The number density of the crystallites could be kept approximately the same as in unheated (fresh) sample by applying of the corona discharge during initial heating step to poling temperature. SHG efficiency in comparison to classic corona poling procedures [5–8] in case of this (first type) poling sequence is increased more then 1.5 times. The maximum enhancement by the first type of orientation sequence was observed in the range of concentrations optimal with respect to SHG efficiency.

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