

## Second harmonic generation from corona-poled polymer thin films of Y-shape chromophore with different isolation groups

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**Abstract.** We characterize thermal stability of second harmonic generation (SHG) properties of four different Y-type polymers poled using corona poling method. These polymers are based on donor–acceptor–donor-type repeating unit with different aromatic moieties acting as donors and dicyanomethylene acting as an acceptor through conjugated bridge. The donor varies from different substituted benzene to phenothiazine. Polymer containing phenothiazine as donor showed higher SHG intensity and high temperature stability due to rigid repeating unit of phenothiazine compared to others with benzene in the main chain.

**Keywords.** Polymer photonics; poled polymers; NLO polymers.

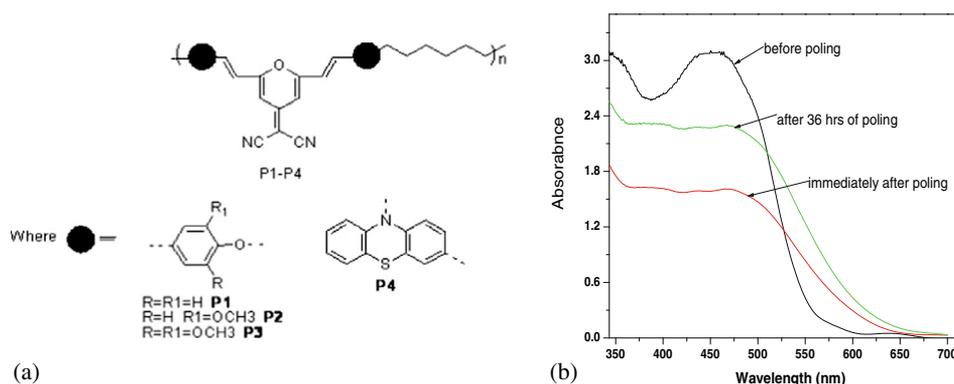
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### 1. Introduction

Poled polymer thin films have become a major focus of scientific research and engineering investigations because of their potential application in photonic devices such as optical modulator, optical data storage, generation and detection of terahertz radiation etc. [1]. Among many interesting properties, the major attraction of poled polymers lies in their large second-order optical nonlinearity. The intrinsic low dielectric constant, ease of processing into thin films, and compatibility with microelectronic processes are the other major advantages of poled polymers. These NLO active poled polymers are obtained either by doping a suitable chromophore molecule into a polymer matrix or by attaching a chromophore covalently to a polymer. However, the as-prepared polymers are isotropic,

i.e. the orientational distribution of NLO chromophores in the polymer is isotropic. To achieve macroscopic NLO activity, for e.g. second-harmonic generation (SHG) or linear electro-optic activity, the chromophores must be oriented non-centrosymmetrically in the polymer matrix. It is achieved by poling, i.e. orientation of dipoles under electric field. Among a variety of techniques for poling, the corona-based electric field poling at elevated temperature (near  $T_g$ , the glass transition temperature of polymer) is an effective and simple technique for producing non-centrosymmetric NLO-active poled polymeric films [2]. One of the challenges in the performance of poled polymer system is the stability of aligned dipoles after poling. It has been observed that with aging and with rise in temperature, the directionality of oriented dipoles is lost leading to poor NLO response. Therefore, efforts are being made to improve the stability of poled polymers. In this context, two approaches to minimize randomization of dipole orientation have been proposed. The first approach is the use of cross-linking and the utilization of high  $T_g$  polymers such as polyimides, polyurethane, etc. In the second approach, NLO chromophores attached in the main chain or side chain have been studied [3]. Main-chain NLO polymers have good thermal stability of dipole alignments, but they often do not dissolve in organic solvents, and their intractability makes them unusable to fabricate stable films. Side-chain NLO polymer systems have advantage of good solubility, homogeneity and high loading level of NLO chromophores, but they often suffer from poor stability of dipole alignments at high temperatures. In recent reports the two approaches were combined to obtain Y-shape molecular architecture of the polymer [4]. Here the pendant NLO chromophores are components of the polymer backbone (figure 1). The Y-shaped polymer is considered to be of advantage as it has shown reasonable enhancement in thermal stability ( $T_g$ ) up to 155°C. The main advantage of the Y shape is the stability similar to linear polymer and a processing ability similar to side chain polymers.

In the present work, we characterize SHG properties of four different Y-type polymers poled using corona poling method. These polymers are based on donor-acceptor-donor-type repeating unit having different aromatic moieties acting as donors, and dicyanomethylene acting as an acceptor through conjugated bridge. Structures of four



**Figure 1.** (a) Basic structure of Y-shape polymer with different side groups (P1-P4). (b) Typical absorption spectrum of polymer P4 before and after poling.

polymers are shown in figure 1a. The donor group is directly linked to the polymer backbone at both the ends and the acceptor dicyanomethylene group is attached to pyran ring. The donor is varied from different substituted benzene to phenothiazine. We studied the influence of four different side groups attached to polymer backbone on the stability of SHG intensity of poled polymer with temperature.

## 2. Film preparation and poling

Synthesis details and their structural characterization using NMR, FTIR and thermal properties are reported elsewhere [5]. For making thin film of these polymers, indium tin oxide (ITO) glass substrates were pre-cleaned with dimethyl formamide (DMF), distilled water, methanol and acetone thoroughly in ultrasonic bath. 3 wt% chloroform solution of the polymer was filtered through  $0.25\mu$  teflon filter to remove undissolved particles and then the solution was spin casted on ITO glass slide with rotation of 1200 rpm for 60 s at room temperature. Finally, the cast films were dried in vacuum for 12 h at room temperature (RT) to remove the trace amount of solvent. Films thickness were measured using KLA-Tencor Alpha-step surface profiler and were  $\sim 1\mu\text{m}$ . Dipolar orientation of polymer was achieved using in-house developed corona poling set-up. For SHG measurements we used Q-switched Nd:YAG laser pulses (1064 nm, 5 ns, 10 Hz rep rate). To avoid damage to polymer samples the laser energy falling on to sample was kept below 1mJ/pulse and was weakly focused to  $\sim 500$  micron beam diameter. The SHG signal was detected using photomultiplier tube (PMT) and fundamental beam from the generated SHG signal was blocked using IR filter. For *in-situ* SHG measurement, i.e. while poling process is on, the desired DC field ( $\sim 5\text{KV/cm}$ ) is first applied and temperature is gradually increased. Near the  $T_g$ , drastic increase in SHG intensity is observed confirming the beginning of dipolar alignment process. Poling process is kept on for 10–15 min (till SHG intensity stabilizes to its maximum). Temperature is then lowered with field still on. Field is switched off after films are cooled to RT. The degree of dipole orientation of poled polymer films was characterized by using UV-Vis spectroscopy. The order parameter ( $\Phi$ ) of the dipole orientation is calculated using equation [5]

$$\Phi = 1 - A_1/A_0, \quad (1)$$

where  $A_0$  and  $A_1$  are the absorbance of the polymer film before and after poling respectively. The maximum value of  $\Phi = 1$  corresponds to 100% alignment of dipoles in the field direction, while  $\Phi = 0$  implies isotropic orientation of dipoles.

## 3. Thermal stability of SHG intensity

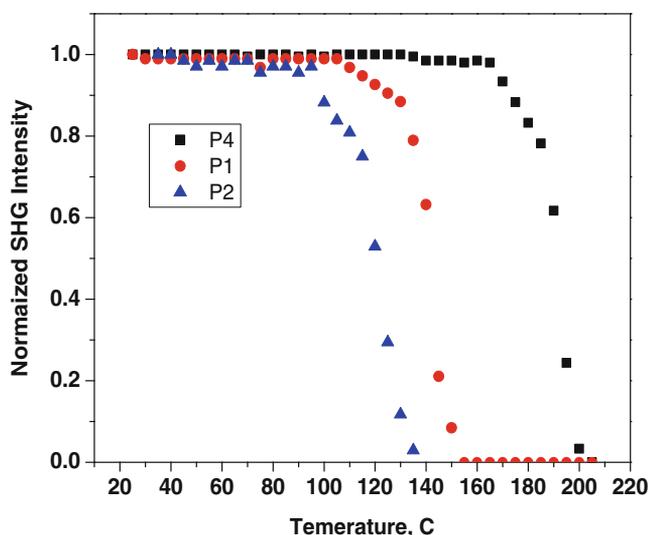
The absorption data of polymer P4 before and after poling are shown in figure 1b. It can be observed from table 1 that the donor structure has influenced the absorption pattern of the polymer as acceptor remained same. The wavelength of maximum absorbance ( $\lambda_{\text{max}}$ ) depends on the conjugation length and donor strength. P4 shows highest  $\lambda_{\text{max}}$  because it has phenothiazine as donor group which is known for maximum donor strength characteristics as compared to other polymers. From the change in absorption due to poling the order parameter ( $\Phi$ ) is calculated and found to be 0.07–0.48 (table 1). Except

**Table 1.** Optical and thermal properties of poled polymers.

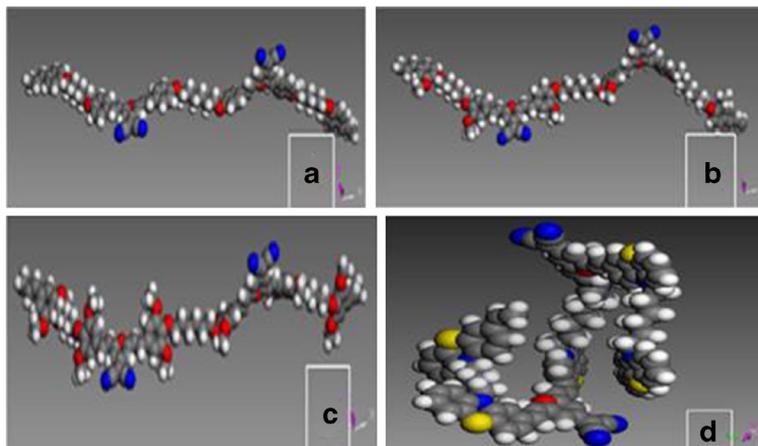
Polymer	$\lambda_{\max}$ (nm)	$T_g$ ( $^{\circ}\text{C}$ )	$\Phi$
P1	417	172	0.30
P2	340	129	0.20
P3	337	133	0.07
P4	459	212	0.48

P3 all other polymers showed high value of  $\Phi$  and sufficient SHG from poled films. Since P3 has two methoxy substituents on benzene ring which leads to large steric effects for dipole orientation. Steric effect here refers to hindrance or obstacle due to large bulky side groups for easy movement of dipolar molecules along the field direction.

For studies on thermal stability, we first poled each polymer for sufficient time to achieve maximum possible SHG intensity. All poled polymer samples were kept at room temperature for more than a week or so and then loaded back to the heating stage for thermal studies. The temperature of the poled film was increased at the rate of  $4^{\circ}\text{C}/\text{min}$  and SHG intensity was monitored. Figure 2 shows the dynamic thermal stability of polymers P1, P2 and P4. It can be seen that SHG intensity of P2 is stable up to  $100^{\circ}\text{C}$  whereas P1 is stable up to  $110^{\circ}\text{C}$ . This may be due to higher  $T_g$  value of P1 compared to P2 (also P3, but which relaxed very fast and attained barely measurable SHG intensity). But when the substituent changes to heteroaromatic moiety containing polymer (P4), the SHG intensity is observed to be highest and remains stable up to almost  $165^{\circ}\text{C}$ . It is also important to know the relaxation behaviour of the poled polymers at ambient condition as it is essential for a device to ensure long term functionality. As polymer P4 shows better dynamic thermal stability, SHG was monitored with time to know the temporal stability.



**Figure 2.** Thermal stability data of poled polymers showing comparison of second harmonic intensity from poled polymers as a function of temperature.



**Figure 3.** PCFF-based simulation results of geometry optimization of polymers (a) P1, (b) P2, (c) P3 and (d) P4.

The measurement was done at room temperature and it was observed that after one month of poling, the SHG intensity decreased. This strong stability of P4 could be due to high  $T_g$  and the nature of phenothiazine as donor substituent.

To examine the effect of different substituent, i.e. mono and di-methoxy-substituted benzene and phenothiazine on the geometry of designed polymers and the resulting stability of NLO properties, we made geometry optimization computational study. The polymer consistent force field (PCFF), developed for synthetic polymers, forms the basis of the simulations [6]. The simulated structures of the polymers are shown in figure 3. The shapes of polymers P1, P2 and P3 are found to be zigzag in nature where repeating unit is Y-type. The acceptor (pull unit) groups and donor (push unit) groups are found orthogonal (opposite regiomers) to each other. The orientation of these groups has large contribution to the net dipole moment and consequently on SHG intensity of the polymer. In the case of P4, although Y shape is maintained, the appearance of the polymer is akin to a ribbon. The calculated energy of synthetic polymers depends strongly on the conformational statistics of the polymer chains and the force field. The energy values are found to be maximum in the case of P3. It is known that having two methoxy substituents on benzene ring, P3 has large steric effect, which might be responsible for high energy value. P1 has the lowest energy value indicating its maximum stability. P4 has the energy slightly higher than P1. Thus, P4 has both high stability and very high electron donating group. This helps to attain high order parameter and stability of SHG signal over a longer period of time.

#### 4. Conclusion

Four Y-type polymers were characterized for their SHG property. The glass transition temperatures of all polymers were beyond 129°C and ranging up to 212°C. These polymers easily formed optical quality films from their chloroform solution. The solid films

remained stable at high electric field (4.8 kV) during poling. The NLO activity could be predicted from order parameter data obtained using UV–visible absorption spectrum. The absorption change due to poling, and particularly for polymer P4 the order parameter was quite high ( $\sim 0.48$ ). Polymer P4 showed higher SHG intensity and high temperature stability due to rigid repeating unit of phenothiazine compared to others with benzene in the main chain.

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