A comparative Poling work on DAN and DR1 doped PC and PMMA polymer thin films

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Abstract

This work consists of a review and a systematical study of the process followed in thermal poling of polymeric thin films. Starting from the preparation of samples, the characterization of the materials used, up to the determination of their linear, nonlinear optical and electrical properties, a series of steps are presented, based on recent literature in this field. Using the available means within the optimum conditions emphasized in the literature, poling experiments on four different guest-host systems were carried out and compared. The results obtained show a significant increase in the degree of alignment of guest molecules in the host polymers with high Tg. Inhomogeneity on the surface of poled films was proven by SEM images and UV-visible absorption spectrum of the poled samples.

Key words: Corona Poling, guest-host polymer, degree of alignment, inhomogeneity

1. Introduction

Polymeric materials continue to be a major focus of scientific research because of their advantages over inorganic crystals and semiconductors. These materials have large electro-optic (EO) coefficient, high response speed and low dielectric constant, are easy to process into thin films, and are compatible with microelectronics.
Poled polymers have potential applications in photonic devices such as optical modulators, optical data storage, generation and detection of terahertz radiation etc.
Poled polymeric organic materials are far better than inorganic crystals at providing high band width and low power consumption which will be needed in future computer systems and mobile devices. Because of the fast development in telecommunication and computer systems, the need of high band width and low power consumption will necessitate data rates of 100 Gbs^{-1} or more. Nowadays, in order to achieve these speeds, valuable research is done on EO polymer/silicon hybrid systems [1,2].
In order to find better EO polymers for different hybrid systems, recently, a lot of work on different kinds of poled polymeric materials is carried out. Some of these works concentrate on the synthesis of new materials with high molecular hyperpolarizability β values [3-5], some of them emphasize the increased poling efficiency [6-8] and others the enhanced long term thermal stability of polar induced alignment [9,10].
Yang et al. synthesized a series of chromophores based on the same bis(N,N-diethyl)aniline donor and the tricyanofuran acceptor (TCF) linked together via the modified thiophene π-conjugation with different isolated groups [3]. They have observed that the high β values of these

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chromophores can be effectively transferred into large electro-optic (EO) coefficients (r_{33}) in poled polymers. The measured β values of three chromophores (y1, y2 and y3) were 713, 652 and 636×10^{-30} esu respectively. It is also reported that the obtained values of the electro-optic coefficient of poled films containing 25% wt of these new chromophores doped in amorphous polycarbonate (APC) are of 149, 139 and 125 pm/V at 1310 nm respectively.

While Shi et al. [4] reported a synthesis of acrylate-based dendron-functionalized cross-linkable NLO chromophores which has quite high β values: 4000×10^{-30} esu at 1.907 μm for C1 and 6000×10^{-30} esu at 1.907 μm for C2 and C3, where Cx are the names of the chromophores used. By using these cross-linkable high β value chromophores, they get very high EO coefficient (as high as 126 pmV^{-1} at 1310 nm) and an alignment stability of up to 200 ℃.

Su Huang et al. reported ultra-large EO coefficients up to 160-350 pm/V at 1310 nm. They used a 50 nm thick TiO_2 layer between ITO and EO polymer. Due to this TiO_2 barrier, they succeeded to apply very high poling fields onto the samples (350 V/μm) and achieved a 100% improvement in the poling efficiency [6]. Thin barrier layer blocks significantly excessive charge injection and reduces the leakage current. Besides TiO_2, inorganic SiO_x networks [7-9], conducting polymer blends of poly(ethylene dioxythiophene) (PEDOT):poly(strenesulfonic acid) (PSS) [10] and sol-gel derived hybrid organic-inorganic glasses are used as barrier layers [11].

In other studies on poling, it is reported that dissolved oxygen interacts with chromophores and reduces the degree of alignment in poled guest-host systems [12]. To avoid this interaction and keep the corona generated ionic composition and conductivity independent of temperature and moisture, ambient air in the corona chamber was replaced by nitrogen [13]. As it is reported by Min and coworkers, the use of nitrogen in the poling chamber reduces greatly the losses in the 2 cm long waveguides. While the measured loss was 4-7 dB in the sample poled in air, no loss has been noticed in nitrogen [12].

In our study, in order to obtain optimum poling conditions a comparative poling work is done on two different guest chromophores: 2-(N,N dimethylamino)-5-nitroacetanilide (DAN) and disperse Red-1 (DR1), doped in two different host polymers: polycharbonate (PC) and Polymethylmethacrylate (PMMA). For making thin films of these polymers, indium-tin-oxide (ITO) glass substrates were pre-cleaned with acetone, dichloromethane and distilled water thoroughly in ultrasonic bath. 10% weight (wt) DAN and DR1 in PC and in PMMA solutions were prepared. Dichloromethane is used since it is a good solvent for both polymers and nonlinear optical (NLO) molecules. Solutions were filtered through a 0.25 μ teflon filter in order to eliminate undissolved particles. Thin films of these materials were prepared by dip coating method. All samples were dried in an oven at 75 ℃ for 12 hours to ensure the removal of the residual solvent. Thickness measurements were carried out using a KLA-Tencor P6 Alpha-step surface profiler. 1.5-2.7 μm thin films were obtained.

For poling, the corona discharge method was used. In order to understand the effect of the needle height on the alignment of chromophores, some samples were poled with a 2 cm needle height and others were poled at a 1 cm needle height. The poling temperature was 85℃ and the poling field was 4.5 kV. Samples were poled for 5 minutes. During the poling process, the leak through current (LTC) was recorded by a Keithley 617 electrometer. UV-visibie absorption spectrums of poled samples were taken by Shimatsu UV-visible 2600 spectrometer. To investigate surface morphology of the poled sample, SEM images of the samples were taken.

3. Results and Discussion

3.1 The Current Density-Temperature Relationship

In order to get current density-temperature relationship of the samples, the LTC was monitored during poling. The samples were heated at a constant ramp rate of 10℃/min.

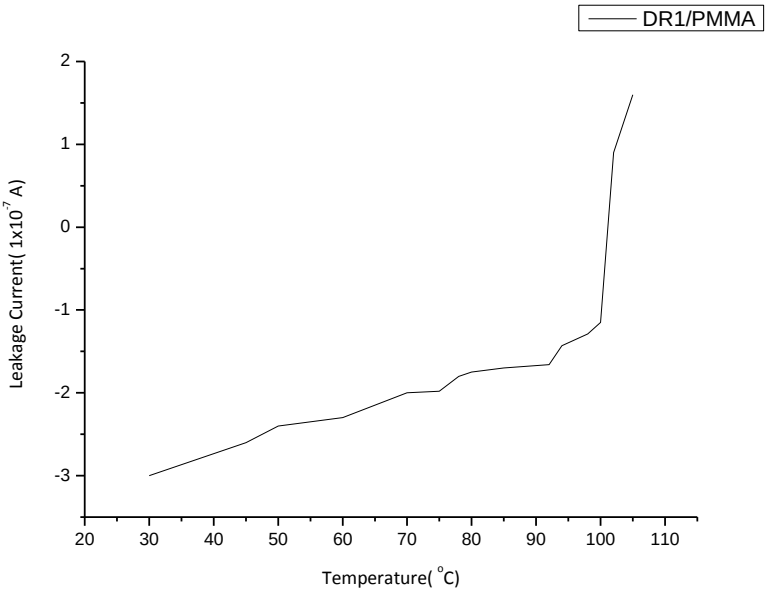


Figure 1. The LTC vs Temperature characteristics of 10% wt DR1/PMMA (heating cycle)

As can be seen in Figure 1, at room temperature LTC increases slowly, but around Tg, a sharp increase occurs. This sudden increase in LTC can be explained by an increase in molecular movements around Tg. Similar leakage current-temperature behaviour has been reported by Xingyu Zhang et al. [14].

The LTC-temperature relationship was observed during the cooling cycle as well. Normally, during the cooling cycle, a reduction in LTC is expected. This fact has been observed in some samples. But in others the LTC continued to increase until a short circuit occurred as seen in Figure 2 below.

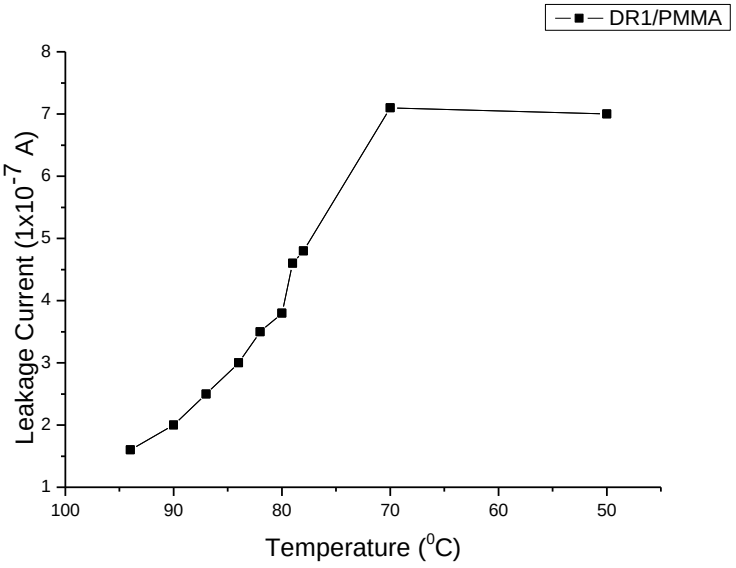
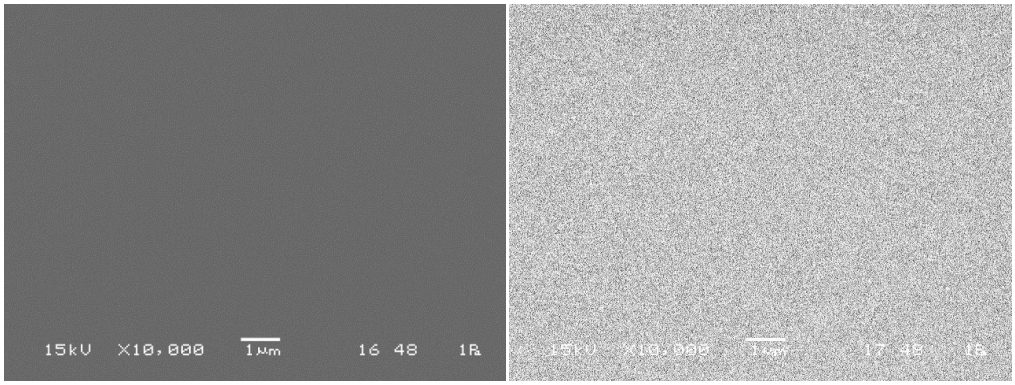


Figure 2. The LTC vs temperature characteristics of DR1/PMMA (cooling cycle)

This increase in LTC may be due to the inhomogeneities that occur on the surface of the sample during poling. The increase of inhomogeneities on the surface damages the films. Nitiss et al. have reported that surface and spatial inhomogeneities in the poled area of the sample appear in certain poling conditions. They have demonstrated that the densities of inhomogeneity depend on the strength of the poling field, the sample temperature and some pre-poling conditions [13]. It has been reported that poling with corona discharge may influence the surface quality of the film which is usually attributed to the bombardment of the film by accelerated ions.
The rate of increase in LTC for cooling is as high as that of heating. The increase is attributed to the surface inhomogeneities but the quite high rate needs further explanation.

3.2 SEM Images of Poled Samples

In Figure 3 the SEM images of DR1 doped PMMA sample before and after poling are shown.



(a) (b)

Figure 3. SEM images of DR1/PMMA sample. (a) before poling, (b) after poling

The surface homogeneity and inhomogeneity of the same sample are clearly seen in figure (a) before poling, and figure (b) after poling respectively. İnhomogeneity is not local, but evenly spreads all over the film surface. This indicates that, rather than being due to ionic bombardment, the inhomogeneity is either chemical or thermal.

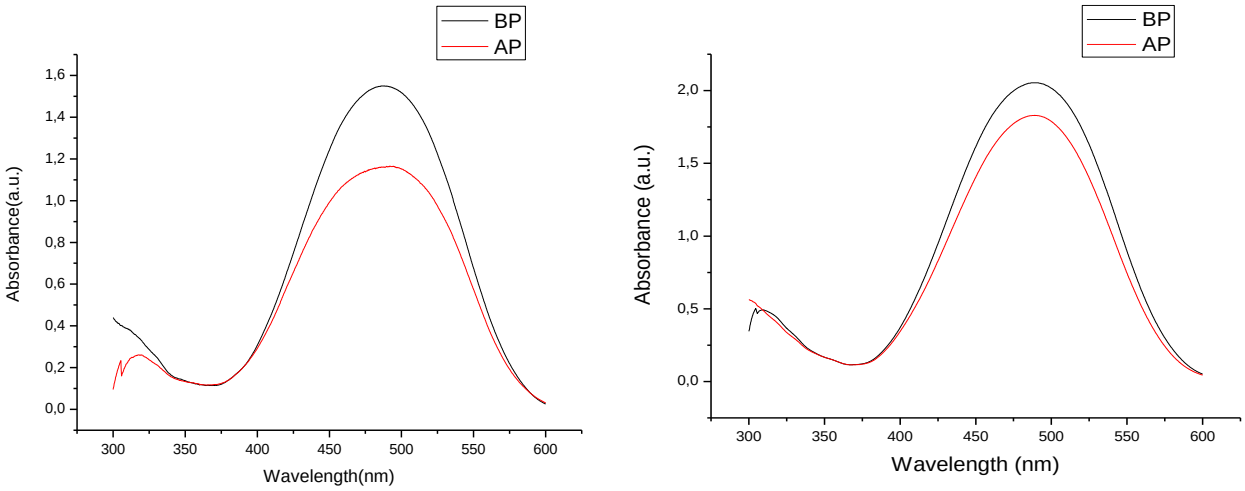
3.3 Order Parameter of Chromophores

The degree of dipole orientation of poled polymer films was characterized by using UV-visible spectroscopy. The order parameter (Φ) of the dipole orientation is calculated using equation

$$\Phi = 1 - \frac{A_1}{A_0}$$

where, A_0 and A_1 are the absorbance of the polymer films before and after poling respectively. The maximum value of Φ=1 corresponds to 100% alignment of dipoles in the field direction, while Φ=0 implies isotropic orientation of dipoles. The absorption spectrum of four samples are taken and shown in Figure 4 and Figure 5.

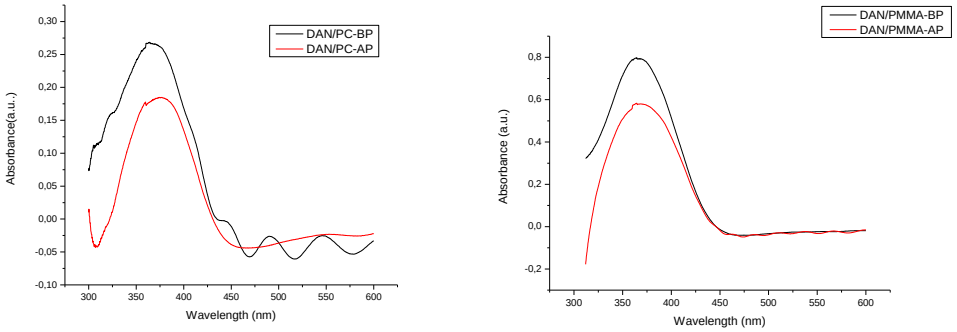
The absorption peak position was λ_{max} = 486 nm for both DR1/PC and DR1/PMMA as seen in Figure 4. This is attributed to $\pi \rightarrow \pi^*$ transitions of the absorption band in DR1 [15]. The difference in peak values of absorption between poled and unpoled samples of DR1/PC and DR1/PMMA in Figure 4, and DAN/PC and DAN/PMMA in Figure 5 is clearly seen. The values of the absorption peak are shown in Table 1 below.



(a) (b)

Figure 4. UV-visible absorption spectrum of unpoled and poled (a) DR1/PC and (b) DR1/PMMA

Another important point that has been observed is the degree of alignment of the same guest molecules in different host polymers. The difference in the degree of alignment is shown in figure (a) and figure (b) for both cases. It is clear that the degree of alignment of DR1 chromophores is higher in PC compared to PMMA. This difference has been noticed in each poling case. A similar difference was also observed in the value of the absorption peak for DAN chromophore. This confirms our previous results [16].



(a) (b)

Figure 5. UV-visible absorption spectrum of unpoled and poled (a) DAN/PC and (b) DAN/PMMA

The order parameter Φ of poled samples was calculated and shown in Table 1. As can be seen in this table, the order parameter of DAN/PC is higher than DAN/PMMA, and Φ of poled DR1/PC is higher than DR1/PMMA. Since the alignment of these two different types of guest molecules in the host PC is higher than in PMMA, and the glass transition Tg of PC is higher than the one of PMMA, we may deduce that the alignment of guest molecules is higher for polymers with high Tg. Recently Joshi et al. have reported higher order parameters in high Tg polymers [17].

Table 1. Optical and thermal properties of poled polymers

Sample	λ_{max} (nm)	Tg of Host Polymer (°C)	Φ
DAN/PC	370	150	0.34
DAN/PMMA	370	110	0.26
DR1/PC	490	150	0.25
DR1/PMMA	490	110	0.11

A confirmation to homogeneity of the surface before poling and inhomogeneity after poling was observed in figure 5 (a). At the wavelength between 450 nm and 600 nm interference fringes occurred which indicates smoothness and homogeneity of the film surface. But, no fringes are seen in the absorption spectrum of the poled sample. This may be a strong sign of inhomogeneity occurrence on the surface after corona poling.

4. Conclusions

In this study, it was confirmed once again that the degree of alignment is higher in high Tg polymers. SEM images of the poled samples revealed that inhomogeneity is not local but all over the sample surface. This result implies that, the inhomogeneity is either chemical or thermal rather than being due to ionic bombardment. An evidence for the formation of inhomogeneity on the surface of the poled samples was obtained in UV-visible absortion spectrum. The interference fringes observed on the surface of the poled sample was not observed on the surface of unpoled sample.
Further thermal studies need to be done in order to find out the origin of inhomogeneity.

References

[1] Xiaolong Wang, Che-Yun Lin, Swapnajit Chakravarty, Jingdong Luo, Alex K.-J. Yen and Ray T. Chen, Effective in-device r_{33} of 735 pm/V on electro-optic polymer infiltrated silicon photonic crystal slot waveguides, Opt Lett 2011;36(6):882-884.

[2] Jingdong Luo, Su Huang, Zhengwei Shi, Brent M. Polishak, Xing-Hua Zhou and Alex K-Y. Jen, Tailored Organic Electro-optic Materials and Their Hybrid Systems for Device Applications, Chem Mater 2011;23: 544-553.

[3] Yang Y, Wang H, Liu F, Yang D, Bo S, Qiu L, Zhen Z, Liu X, The synthesis of new double-donor chromophores with excellent electro-optic activity by introducing modified bridges, Phys Chem Chem Phys 2015;17: 8

[4] Zhengwei Shi, Jingdong Luo, Su Huang, Brent M. Polishak, Xing-Hua Zhou, Shawna Liff, Todd R Younkin, Bruce A Block and Alex K -Y Jen, Achieving excellent electro-optic activity and thermal stability in poled polymers through an expeditious crosslinking process, J Mater Chem 2012; 22; 951-959

[5] Yue Jia, Andrew M. Spring, Feng Yu, Kazuhiro Yamamoto, Isao Aoki, Akira Otomo, Shiyoshi Yokoyama, A norbornene polymer brush for electro-optic applications, Thin Solid Films, 2014;554:175-179.

[6] Su Huang,Tae-Dong Kim, Jingdong Luo, Steven K Hau, Zhengwei Shi, Xing-Hua Zhou, Hin-Lap Yip and Alex K-Y Jen, Highly efficient electro-optic polymers through improved poling using a thin TiO_2- modified transparent electrode, Appl Phys Lett 2010; 96:243311

[7] M Sprave, R Blum and M Eric, Appl Phys Lett 1996; 69: 2962

[8] H Chen, B Chen, D Huang, D Jin, J D Luo, AK –Y Jen and R Dinu, Appl Phys Lett 2008;93: 043507

[9] R Blum, M Sprave, J Stablony and M Eich J Opt Soc Am B 1998;15: 318

[10] J P Drummond, S J Clarson, JS Zetts F K Hopkins and S J Carraci, Appl Phys Lettn1999; 74: 368

[11] C T DeRose, Y Enami, C Loychik, R A Norwood, D Mathine, M Fallahi, N Peygamberian, J D Luo, A K –Y Jen, M Kathaperumal and M Yamamoto, Appl Phys Lett 2006; 89: 131102

[12] Min-Cheol Oh, Hua Zhang, Cheng Zhang, Hernan Erlig, Yian Chang, Boris Tsap, Dan Chang, Attila Szep, William H Steier, Harold R Fetterman, and Larry R Dalton, Recent advances in electro-optic polymer modulators incorporating highly nonlinear chromophore, IEEE 2001;7(5):826-835

[13] Edgars Nitiss, Eduards Titavs, Karlis Kundzins, Andrej Dementjev, Vidmantas Gulbinas and Martins Rutkis, Poling Induced Mass Transport in Thin Polymer Films, J of Phy Chem B 2013;117: 2812−281**9**

[14] Xingyu Zhang, Amir Hosseini, Jingdong Luo, Alex K-Y Jen and Ray T Chen, Wide optical spectrum range, sub-volt, compact modulator based on electro-optic

polymer refilled silicon slot photonic crystal waveguide, Opt Lett 2013;38(22): 4931-4934

[15] A Sugita, Y Sato, K Ito, K Murakami, Y Tamaki, N Mase, Y Kawata, and S Tasaka, Second-Order Nonlinear Optical Susceptibilities of Nonelectrically Poled DR1−PMMA Guest−Host Polymers, J Phys Chem B 2013;117,14857-14864

[16] Y Karakus, D Bloor, G H Cross, Enhanced linear electro-optic response and enhanced stability of thermo-poled ‘guest-host’ polycarbonate thin films, J Phys D: Appl Phys 1992; 25:1014-1018

[17] M P Joshi, S R Mohan, B Kolli, S P Mıshra, A K Palaı, T Kanaı, T S Dhami, L M Kukreja and A B Samui, Second harmonic generation from corona-poled polymer thin films of Y-Shape chromophore with different isolation groups, PRAMANA, Journal of physics 2014;82,(2): 283-288.