

Chapter 5 Results and Discussion

5.1 Nonlinear optical properties of polymer films

The nonlinear electro-optical response of condensed matter is extremely small but the existence, character, and magnitude of these nonlinearities provide more detailed information about the structure of matter. Light is electromagnetic waves, however the field intensities of ordinary light waves are so low that nonlinearity effects are not apparent. In order to have a finite second-order susceptibility, a polymer system must orient in such a way that the total system does not possess a center of symmetry. This is most easily accomplished by applying an electric field at a temperature where the dipoles can be readily oriented. High field strength is obtained using electrode poling of pure thin PPO film and electrode design. Electrode poling is compatible with electro-optic and second harmonic device processing requirements. When sufficient strength of static electrical field is applied to the media to perturb their refractive properties, Kerr or Pockel electro-optical effects are demonstrated.¹ The Kerr effect was discovered in amorphous substances that are isotropic and become doubly refracting when subjected to strong electrical fields. The Pockel effect discovered in several crystals is much weaker. Isotropic crystals become uniaxial and uniaxial crystals become biaxial in a steady electrical field with sufficient intensity.¹

A dielectric material is both electrically and mechanically isotropic before applying electrical field. When an electrical field is applied to this material, it is subjected to internal stress and thus electrets extend along the electrical field direction as the result of these electrical stresses. This effect is termed electrorestriction. One cannot generate an electrical field simply by applying mechanical pressure. The deformation involves density changes, with corresponding changes in dielectric constant or the refractive index. The magnitude of the deformation depends not only on the elastic modulus of the medium, but also on dielectric constant and density. However in some crystals, there is another component called piezoelectric effect that does have an inverse effect. Mechanical deformation does give rise to an internal electric polarization proportional to the strain. The polarization arises from unequal displacements of different ion species composing the lattice of the solid. Generally, these electrically generated stresses give

rise to mechanical deformation, or strain, creating the opposing stresses that will reestablish equilibrium.

The field induced thickness change can be modeled by the following equation:

$$Z(E) = Z_0(1+dE+aE^2+\dots) \quad (5.1)$$

Where Z is the film thickness under electrical field. Z_0 is the initial thickness without electrical field. d is the piezoelectric constant and a is the electrostriction constant of the polymer electrets. E is the electric field vector. The piezoelectric and electrostriction effects are expanded in equation 5.2. This electrostriction is proportionally to E^2 . The piezoelectric effect is directly proportional to E .²

For an alternating electrical field, the electric field vector can be express as: $E=E_0\cos(\omega t)$, substituting into equation 5.1, the following expression can be obtained.

$$\Delta Z(E)/Z_0=1/2aE_0+dE_0\cos(\omega t)+1/2aE_0^2\cos(2\omega t) \quad (5.2)$$

Equation 5.2 indicates that the piezoelectric effect is proportional to the frequency (ω) term and the electrorestrictive effect is proportional to the frequency (2ω) term. As we discussed in chapter 3, the first order sidebands are the signals at (carrier frequency $\pm \omega$), and the second order sidebands are the signals at (carrier frequency $\pm 2\omega$).

Figure 5.1 shows the picture of the tracing signal in spectrum analyzer for 3% PPO 2000 at 24kHz electric field frequency. The center peak 1 is the carrier signal at Bragg cell modulating frequency 80MHz. The peaks 3 and 2 are called the first order sidebands. They are at (carrier frequency 80MHz \pm 24kHz). The peaks 6 and 7 are called the second order sidebands. They are at (carrier frequency 80MHz \pm 48kHz).

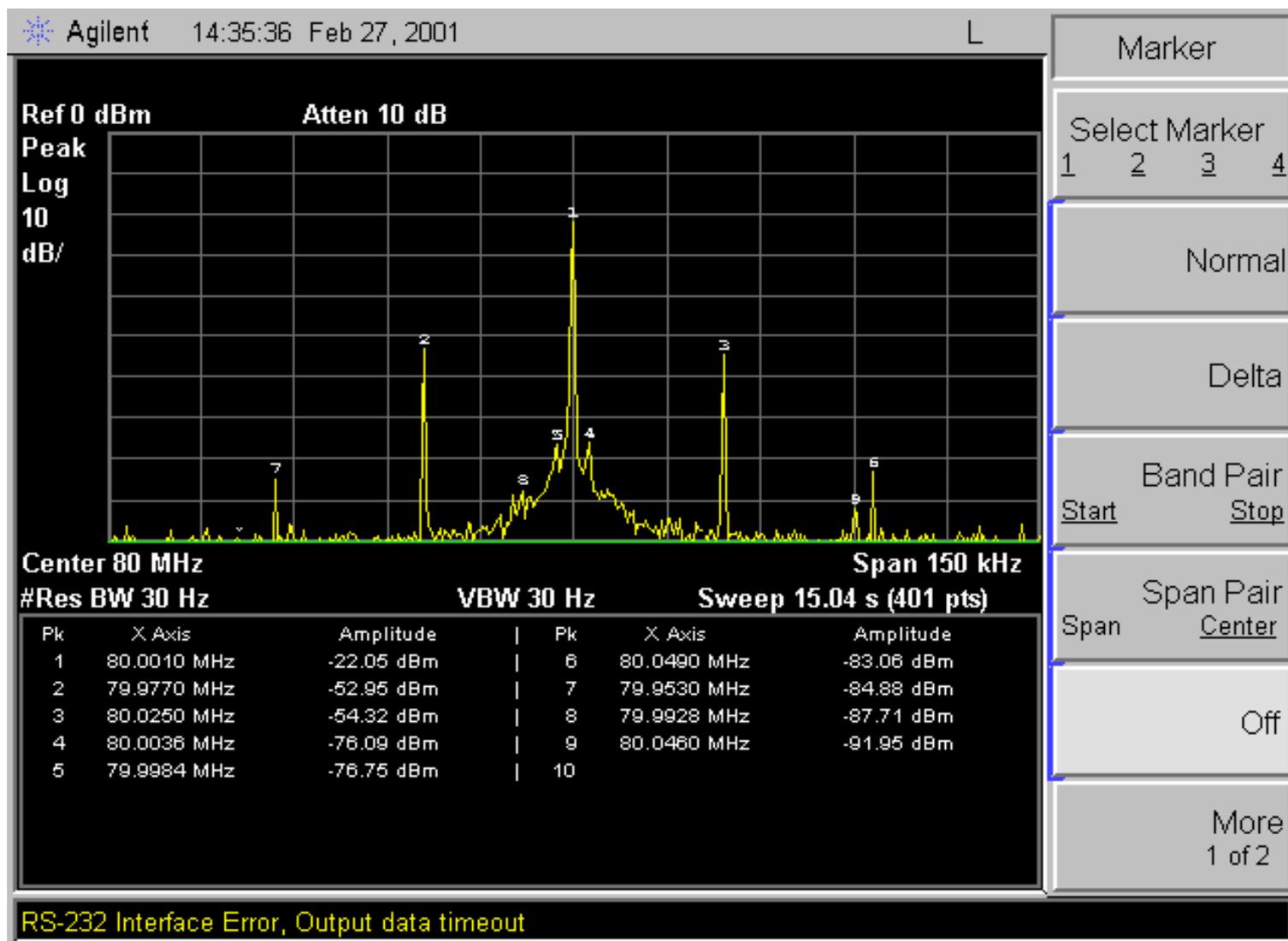
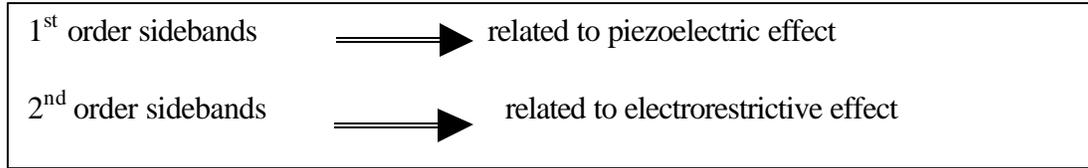


Figure 5.1 Tracing signal of spectrum analyzer with AC frequency at 24kHz fro 3% PPO 2000

Thus,



The electrical effect (piezoelectric and electrorestrictive) was probed by the optical length change of laser passing through polymer film by heterodyne interferometry. Define n as the refractive index along the laser electric field which is parallel to applied electric field. Z is the instantaneous thickness of polymer film at a given applied electric field. $\Delta(nZ)$ is the changes of refractive index along the field direction times instantaneous film thickness. $\Delta(nZ) = n\Delta Z + Z\Delta n$. Typically for polymers, the birefringence is $\sim 0.005-0.01$. For thickness of 300nm film, if $\Delta(nZ) = 25\text{nm}$, substitute typically birefringence value for polymers, we can get $Z\Delta n \approx 1.5-3\text{nm}$, $n\Delta Z \approx 23.5-22\text{nm}$. Therefore, we can see that $n\Delta Z$ contributes the most in $\Delta(nZ)$. Especially when we apply high electric frequency, the birefringence of PPO is very small due to its chain orientation. Thus, it is reasonable to assume that the thickness change contribute the most of $\Delta(nZ)$.

5.2 PPO electrical properties

Takeo Furukwa first investigated the piezoelectric property of PPO in 1969.³ PPO films were cast from benzene solution and then elongated by 50% of its original length. The degree of crystallinity was about 40%. The film size was about 5mm×10mm×0.05mm. Brass foils were used as electrodes to attach to the center of both faces of the elongated film. One end was clamped and the other end was given an oscillational stress at frequency 20Hz.³ The discovery of piezoelectric effect of PPO was ultimately related to the asymmetric configuration of macromolecules and it was hypothesized that many other optically active polymers may possess piezoelectric effect.

This work also shows the piezoelectric and Kerr effect under relatively high frequency in PPO. PPO thin film has Kerr effect due to high dipoles that orient in the

electric field direction. The asymmetric polar groups of PPO give the molecules a net dipole moment under electrical field. The orientational polarization of PPO depends on its chemical and physical structure $(-O-CH(CH_3)CH_2-)_n$. The molecular and chain polar structure of PPO is shown in figure 5.2a and 5.2b. We can see the unsymmetric structure of PPO will allow PPO molecules to have a net dipole moment under electric field leading to electro-optical properties.

PPO thin films were found to respond to electric field at kilohertz range. Part of reasons for this fast response is the low glass transition temperature of PPO (about -60°C). At room temperature, the polymer molecules are liquid.

In this work, the refractive index of PPO molecular weight 8000 (referred as PPO 8000) is 1.453. PPO molecular weight 2000 (referred as PPO 2000) was not characterized and here we assumed it has the same refractive index as PPO 8000. All the films thickness for different concentration was measured by AFM as discussed in section 3.1.4. The thickness was described in Table 5.1.

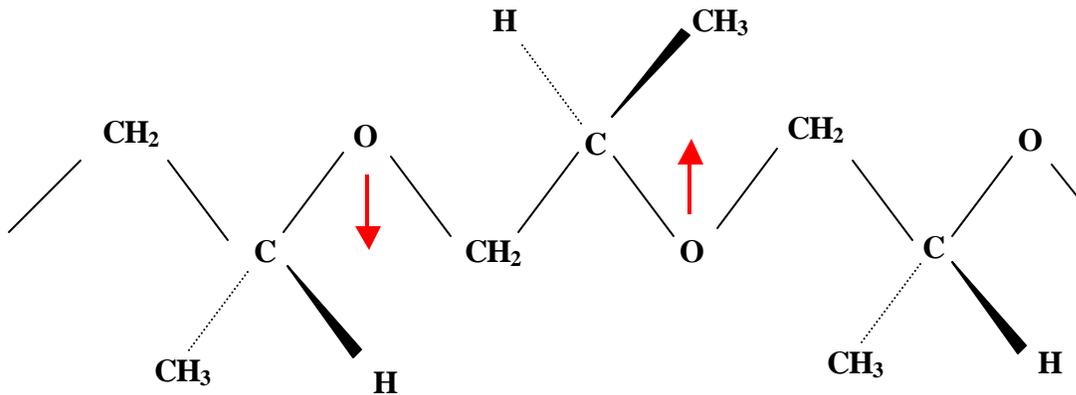


Figure 5.2a PPO molecular polar structure.

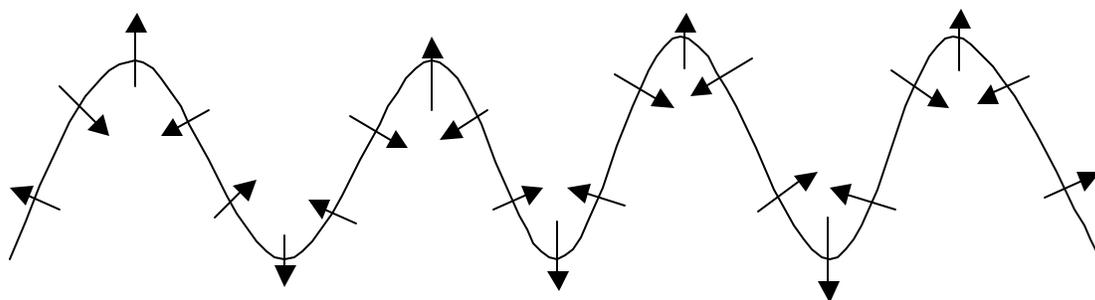


Figure 5.2b PPO chain polar structure

*The dipole moments of PPO bonds are marked by arrows.

The electrical effect on the different concentration and different molecular weight PPO thin films was probed. 4% PPO 2000 has very little electrical effect due to its much larger thickness and thus much lower surface mobility. 2% PPO 2000 also shows very small electrical effects. Concentration less than 2% for PPO 2000 was probed and found to have no electrical effect due to the fact that the $\Delta(nZ)$ is too small to be measurable by our system whose resolution is $\sim 0.5\text{\AA}$. Therefore, we probed 2% PPO 2000, 3% PPO 2000. We also probed the molecular entanglement effects on polymer chain mobility. Thus, 2% PPO 8000 were studied because 3% PPO 8000 did not exhibit any electrical effect. The effect of film thickness on polymer chain surface mobility and their electrical effects are further discussed in this chapter.

Table 5.1 Film thickness of different concentration and different molecular weight PPO measured by AFM

Volume Concentration	Molecular Weight of PPO	Film Thickness (nm)
2%	2000	60 ± 3
3%	2000	103 ± 5
4%	2000	300 ± 15
2%	8000	313 ± 16
3%	8000	420 ± 21

In this research, **PPO was found to respond to electric field at kilohertz range.** The responses are not standing wave resonance due to material geometry. Since the film thickness of these films tested are about 60nm ~ 313nm, and stimulus frequency is at 12kHz~108kHz, the velocity for resonance will be $\sim 10^{-2}$ m/s is unrealistically small. The mechanical resonance of polymer film can be calculated as $v = \sqrt{\frac{\mu}{\rho}}$. μ is the bulk modulus of polymer film and ρ is the density of PPO. Typically, polymer bulk modulus is ~ 2000 MPa and $\rho = 1.0$ g/cm³. Therefore, we can calculate the mechanical resonance velocity for PPO is about 1.4×10^5 cm/s. Therefore, we can justify that the multiple peaks in figure 5.3 and 5.4 are due to material properties instead of material geometry. Therefore, we probe 12kHz and 24kHz since the material shows its highest electrical effects at these frequencies at different electrical field amplitude. We also probed other polymer films deposited on silicon wafer including: PB (polybutadiene), PS (polystyrene), PVDF, PEO (polyethylene oxide), poly(4-vinylpyridine). There were no responses for the above polymer films. This proves that the electrical effect of PPO is not a capacitor effect due to the structure of the device but due to material structure.

Figure 5.3 to 5.9 shows the electrical effects of different concentration and molecular weight PPO thin films. The electrical effect including piezoelectric (film thickness change) and electrorestrictive (polymer chain orientation) effects were measured through the $\Delta(nZ)$ as defined in section 5.1.

5.3 Electrical field frequency effect on PPO electrical properties

The piezoelectric effect and the electrorestriction effect were investigated as a function of applied electric field frequency. Figure 5.3 and 5.4 compares the $\Delta(nZ)$ at 220kV/cm due to the first order (piezoelectric effect) and second order (electrorestrictive effect) sidebands respectively versus frequency for 2% PPO 2000, 3% PPO 2000, 4% PPO 2000 and 2% PPO 8000 films. Figure 5.3 and 5.4 shows the frequency range of all four types of PPO film responding frequency to applied field. These films show piezoelectric and electrorestrictive effects under kHz range. This contrasts with other piezoelectric polymers of which most respond to electric field at Hz. This fast response

of PPO may bring up more opportunities for its application in sensors and other optoelectronic devices.

Figure 5.3 shows that 3% PPO 2000 film has the largest $\Delta(nZ)$ due to the first order sidebands and responds to the largest frequency range. All the films exhibit a local resonance peak around 24kHz. This indicated that 24kHz are the molecular resonance frequency of PPO. We can also see from figure 5.3 that the 2% PPO 8000 has the smallest $\Delta(nZ)$ than all the other three films under the same field. Its responding range is also the smallest from 10kHz to 36kHz. The 2% PPO 2000 film shows a larger $\Delta(nZ)$ than 2% PPO 8000 but much less than 4% PPO 2000 and 3% PPO 2000 films. The responding frequency of 2% PPO 2000 is larger than 2% PPO 8000 and 4% PPO 2000 films ranging from 2kHz to 65kHz. 4% PPO 2000 film has larger changes in $\Delta(nZ)$ than 2% PPO 2000 and 2% PPO 8000 but much smaller than 3% PPO 2000 film. The responding frequency for 4% PPO 2000 film is the second smallest ranging from 6kHz to 44kHz. Higher molecular weight PPO 8000 has more entanglements between polymer molecules and thus requires much longer relaxation time than PPO 2000. The longer relaxation of 2% PPO 8000 chains can not move as fast as the applied electrical field and thus, exhibits the smallest $\Delta(nZ)$ due to the first order sidebands and also the smallest frequency responding range. The 4% PPO 2000 film is the thickest among these films. However, it did not show the largest $\Delta(nZ)$. This is because the thicker film reduces its polymer chain surface mobility dramatically. ~300nm is the critical thickness for polymer chain surface mobility. When polymer chains become sluggish, their piezoelectric effect will reduce at higher frequency. However, the measurement is based on the absolute value of $\Delta(nZ)$, the original thickness contributes to the $\Delta(nZ)$ and this is why 3% PPO 2000 and 4% PPO 2000 films have much larger changes than 2% PPO 2000 film.

Figure 5.4 compares the $\Delta(nZ)$ due to the second order sidebands versus frequency at 220kV/cm for 2% PPO 2000, 3% PPO 2000, 4% PPO 2000 and 2% PPO 8000. Contrasting the data in figure 5.3, the $\Delta(nZ)$ due to the electrorestriction is much larger than the changes caused by piezoelectric effect. The maximum $\Delta(nZ)$ peaks exhibit at 12kHz range. This is exactly half of the resonance frequency for piezoelectric

effect. This confirms that 24kHz are the molecular resonance frequency. The 3% PPO 2000 film exhibits the largest $\Delta(nZ)$ due to the second order sidebands. Second order sidebands are related to the electrorestriction as discussed in section 5.1. The $\Delta(nZ)$ of 3% PPO 2000 ranges from 4nm to 33nm and the responding frequency to the applied field ranges from 2kHz to 80kHz. The 2% PPO 8000 and 2% PPO 2000 films have similar levels of $\Delta(nZ)$ except that 2% PPO 8000 film responds to larger frequency range than 2% PPO 2000 film. The 4% PPO 2000 film has a larger $\Delta(nZ)$ due to second order sidebands, however it responds to the smallest electric frequency range from 3kHz to 22kHz. The initial films thickness of 3% PPO 2000, and 4% PPO 2000 contribute to its larger $\Delta(nZ)$ number than 2% PPO 2000 since the measurement is absolute value of $\Delta(nZ)$. The 2% PPO 8000 film has relatively smaller electrical effects than 3% PPO 2000 and 4% PPO 2000 films at lower frequency. This is due to its higher molecular weight and therefore its higher entanglement between the polymer chain molecules.

The 3% PPO 2000 film is about 300nm thick and 4% PPO 2000 is above 400nm as listed in Table 5.1. Therefore, it is interesting to probe the film thickness effect on the polymer chain surface mobility. This effect has been observed in both piezoelectric and electrorestrictive effects. Table 5.2 compares the maximum $\Delta(nZ)$ and the maximum responding frequency for different thickness film. The 3%PPO 2000 film exhibits the largest $\Delta(nZ)$ for both piezoelectric and electrorestrictive effect of all these films tested. The reasons for this performance were discussed in figure 5.3 and 5.4.

Table 5.2 Comparison of the maximum $\Delta(nZ)$ at certain frequency range for different thickness and molecular weight PPO film

Vol. Conc.	Mol. Wt	Film Thickness (nm)	Responding frequency for piezoelectricity (kHz)	Max $\Delta(nZ)$ due to piezoelectricity (nm)	Responding frequency for electrostriction (kHz)	Max $\Delta(nZ)$ due to electrostriction (nm)
2%	2000	60	10-37	0.36	7.39	10-28
3%	2000	103	2-83	5.33	28.79	2-80
4%	2000	300	6-44	2.07	16.5	4-22
2%	8000	313	15-36	0.32	7.3	11-37

The influence of surfaces on the dynamics of thin polymer films has attracted significant attention in the past decade.^{4,5} Surface properties such as glass transition temperatures (T_g), liquid-crystal melting points, and surface mobility have important technological implications in the areas of adhesion, alignment of liquid crystals, and biocompatibility of polymers.⁶ A variety of experimental studies have established that surface-polymer interactions greatly influence the T_g of ultra-thin polymer films.⁷ These studies involved measurements of an average physical property such as film thickness, using ellipsometry⁴ and X-ray reflectivity, or relaxation times using dielectric⁸ and optical probe techniques.⁹ These properties are found to be influenced by both the polymer-solid and the polymer-air interfaces.⁷ C. S. Hou also investigated the substrate effects for inorganic film $Pb_{0.6}Sr_{0.4}TiO_3$ deposited on different substrates.¹⁰ X-ray diffraction results show that the structure and the lattice of parameters of the substrate greatly influence the growth of the inorganic film. Forrest has shown that free-standing Polystyrene (PS) films have a dramatic decrease in T_g as the film thickness approaches polymer molecular dimensions.⁵ The drop in T_g has been explained by higher mobility at the polymer-air interface than in the bulk. Other experiments on supported films reveal either an increase or decrease in thin film T_g depending on the influence of the polymer-air interface, the chemical composition of the polymer, and the supporting solid substrate.^{4, 5, 8} This research shows the same phenomena of the surface mobility of PPO film. To support this theory, 80nm thick PS film was spin-cast on top of piezoelectric film PPO 2000. This top layer of PS damps both the piezoelectric and electrorestrictive effects out.

5.4 The effect of electric field intensity on polymer electrical properties

Figure 5.5 to Figure 5.10 shows the electric field strength effect of polymer electrical properties. Figure 5.5 compares the $\Delta(nZ)$ due to the first order sidebands as a function of electric field amplitude at 12kHz and 24kHz for 2%PPO 2000. The first sidebands are related to piezoelectric effect as discussed in section 5.1. PPO film does not show any piezoelectric effect until the electric field strength reaches about 123kV/cm for 24kHz and 134kV/cm for 12kHz. At the same electric field amplitude, PPO shows much larger piezoelectric effect at 24kHz than at 12kHz. The piezoelectric effect increases with

electric field strength. The applied external force must be larger than the constraints that polymer molecules place on the motion of electrons in order to break the equilibrium position of the dispersion electrons and give rise to the internal electric polarization proportional to the strain leading to piezoelectric effect. PPO molecules also exhibit resonance response at certain frequency as shown in figure 5.3. Therefore, the larger movement of the polar molecules leading to the larger piezoelectric effect is observed when the applied frequency is close to the molecular resonance frequency. Figure 5.5 indicated that 24kHz is closer to the molecular resonance frequency than 12kHz.

The film thickness and molecular weight effect on the piezoelectricity of PPO films are investigated. The electrical effect of thicker PPO 2000 and PPO 8000 film are not observed. Table 5.1 listed the film thickness for different concentration PPO. The $\Delta(nZ)$ for 3% PPO 2000 and 2% PPO 8000 films were measured as a function of electric field at 12kHz and 24kHz and compared with 2% PPO 2000 film in figure 5.6, 5.7, 5.8 and 5.9. At 12kHz, 2%PPO 8000 does not exhibit first order sidebands. Thus figure 5.6 compares the $\Delta(nZ)$ of 2%PPO 2000 and 3% PPO 2000 films at 12kHz with respect to electric field strength. The $\Delta(nZ)$ of both 2%PPO 2000 and 3% PPO 2000 increases with electric field strength. However, the $\Delta(nZ)$ of 3% PPO 2000 increases much more dramatically than 2% PPO 2000 with electric field. The magnitude difference for $\Delta(nZ)$ of 2% and 3% PPO 2000 is due to their thickness difference that is listed in table 5.1. At 24kHz, 2% PPO 8000 exhibits small first order sidebands. Figure 5.7 compares the $\Delta(nZ)$ due to the first order sidebands at 24kHz for 2%PPO 2000, 3% PPO 2000 and 2% PPO 8000. The $\Delta(nZ)$ for 2% PPO 2000 and 2% PPO 8000 films are less than 0.25nm, the $\Delta(nZ)$ for 3% PPO 2000 film reaches 5.5nm. Since interferometry measures the absolute changes of optical length $\Delta(nZ)$ at the sample, the original films thickness plays a big role at the total magnitude of $\Delta(nZ)$. Table 5.1 shows that 3% PPO 2000 film is 72% thicker than 2% PPO 2000 film. Therefore, $\Delta(nZ)$ for 3% PPO 2000 film is an order of magnitude larger than 2% PPO 2000 film. However this does not apply to 2% PPO 8000. According to Table 5.1, 2% PPO 8000 is much thicker than 2% PPO 2000. Its $\Delta(nZ)$ is about the same as 2% PPO 2000. The reason is that the higher molecular weight causes much higher viscosity and much stronger entanglements between polymer molecules which lead to

much slower and smaller electrical effects for PPO 8000. PPO exhibits the maximum electrical effect at 24kHz further proving that this frequency is the molecular resonance frequency. The possible explanation for this would be higher molecular weight of PPO has much stronger molecular entanglement than smaller molecular weight PPO.

Therefore at 12kHz, PPO 8000 molecules place constraints on their electrons that are so strong that the electrons cannot be polarized under the electric field like PPO 2000 films. While under 24kHz, the polymer molecules have higher motions due to the external frequency being close to their resonant frequency. Even so, the polarization of those electrons is still very small.

Another interesting phenomenon is shown in figure 5.8 and 5.9. The 2% PPO 2000 film does not have second order sidebands at both 12kHz and 24kHz whereas the 2% PPO 8000 and 3% PPO 2000 films both do at these frequencies. According to the previous discussion, the $\Delta(nZ)$ due to the second order sidebands corresponds to the electrorestrictive properties of PPO films. Figure 5.8 and 5.9 compares the $\Delta(nZ)$ due to the second order sidebands for 3% PPO 2000 and 2% PPO 8000 films as a function of electric field strength at 12kHz and 24kHz. Since $\Delta(nZ)$ is directly related to film thickness. The larger thickness 2% PPO 8000 (~ 300nm) is supposed to exhibit larger $\Delta(nZ)$ than 3% PPO 2000 (~103 nm). However, its $\Delta(nZ)$ at both 12kHz and 24kHz is much smaller than that of 3%PPO 2000. With higher electric field amplitude, the electrorestriction effect for the 3% PPO 2000 film increases dramatically while the 2% PPO 8000 film increases much less. This phenomenon maybe explained by the difference in the mechanical properties of these two PPO films. PPO 8000 film has higher molecular entanglements and thus larger modulus than that of 3% PPO 2000 film. The magnitude of electrorestriction is directly related to the modulus of polymer film. All these cause the 2% PPO 8000 film to have smaller electrorestrictive effects than the 3% PPO 2000 film. This explanation is consistent with the fact that the 2% PPO 8000 film needs much higher electric field strength to induce electrorestriction effects than 3% PPO 2000.

Figure 5.9 compares the $\Delta(nZ)$ due to electrorestriction versus electric field for 3% PPO 2000 and 2% PPO 8000 films at 24kHz. The $\Delta(nZ)$ due to electrorestriction for 2% PPO 8000 and 3% PPO 2000 reaches 5.8nm and 8.2nm respectively. The

electrorestriction effects increase with higher electric field strength. Compared with data shown in figure 5.8, the $\Delta(nZ)$ for 2% PPO 8000 at 12kHz and 24kHz are very close. 2% PPO 8000 film has a smaller dependence on frequency. The 3% PPO 2000 shows much larger changes of $\Delta(nZ)$ at 24kHz than at 12kHz. This indicates that the electrorestrictive effect for 3% PPO 2000 responds to electric field strength much effectively at 12kHz than at 24kHz. This also indicates that electrorestriction has smaller dependence on molecular resonant frequency than piezoelectric effect.

Figure 5.10 compares at the $\Delta(nZ)$ due to first order sidebands versus frequency for 2% PPO 8000 at two different electric field intensity. At 220kV/cm field, the maximum $\Delta(nZ)$ peak located at 24kHz, however this peak shifts to about 25kHz at 200kV/cm. This justified that electric field intensity affect the local resonance frequency.

5.5 Direct measurement of PPO film thickness change under electric field

The propagation of light takes place in the form of electromagnetic waves.¹¹ For our purpose, we can consider only the periodic changes of the strength of the electrical field. In a beam of light, the planes of vibration may assume all orientations and the light may have all states of polarization. Therefore, when we place a dichroitic polarizer in front of the laser beam source, the dichroitic polarizer will transmit only light with the one plane of vibration that corresponds to the polar's own plane of vibration.¹¹ All light entering a polarizer will immediately be split into two components: one parallel to the polar's plane of vibration, the other perpendicular to the polar's plane of vibration. The first is transmitted and the second is eliminated. Therefore, when we measure the $\Delta(nd)$ with polarizer, the electrical field of the polarized light is parallel to applied electric field in which the polymer chains orient. Thus, the differential interferometer will be able to measure the birefringence or the Kerr effect when the polarizers are removed. Without polarizers, the laser beam will no longer be polarized parallel to the applied electric field direction in which polymer chains orient. Thus, the polymer birefringence effect of polymer can be neglected and the optical length change at the sample film is only contributed by the film thickness change. This enables us to measure film thickness change directly from this interferometer.

Table 5.3 compares the $\Delta(nZ)$ with and without polarizer for 3% PPO 2000 and 2% PPO 8000 films under 220kV/cm at 12kHz and 24kHz respectively. In general for both 3% PPO 2000 and 2% PPO 8000 films, the $\Delta(nZ)$ with polarizer is smaller than that without polarizer. The negative sign for the $\Delta(nZ)$ indicates that the polymer chains are pulling down to the sample surface which is parallel to the applied electric field. This results in a decrease of film thickness. The $\Delta(nZ)$ is smaller with birefringence effect considered than that without. This means that the polymer chains become more oriented under electric field and therefore the refractive index increases while the film thickness decreases under external field. Compare 2% PPO 8000 film at 24kHz with polarizer and without polarizer, the difference in the $\Delta(nZ)$ between the above two conditions is very small. This indicates that the film thickness change contributes almost all of the optical path changes in the sample and there is no obvious birefringence effect in 2% PPO 8000 at 24kHz. The optical anisotropy induced in larger organic molecules results largely from alignment of electrically anisotropic molecules. It can attain the full magnitude only in electrical fields that vary slowly, so that the molecular dipoles can follow the field. In other words, polymer dipoles are unable to orient with high frequency electric field due to the polymer chain relaxation. The birefringence effect is much smaller at 24kHz than at 12kHz. 3% PPO 2000 film has similar results to 2% PPO 8000. Table 5.3 also indicates that 24kHz is the molecular resonance frequency due to the maximum film thickness change at 24kHz.

Most of the films were spin-cast on hydrophilic silicon substrate. Due to the high polarity of PPO molecules, there are chemical bonds formed between the polymer chain and the substrate. These strong bonds serve as the anchors of the polymer chains on the solid substrate when external electric force is exerted on polymer molecules. This anchoring effect is very critical for polymer films to exhibit piezoelectric and electrostrictive effects. An experiment was performed based on testing the effect of substrate on the polymer chain dynamics. The silicon substrate was treated into hydrophobic and then PPO film was spin-cast on top of the substrate. There were no sidebands. This proved the anchoring effect of the silicon substrate.

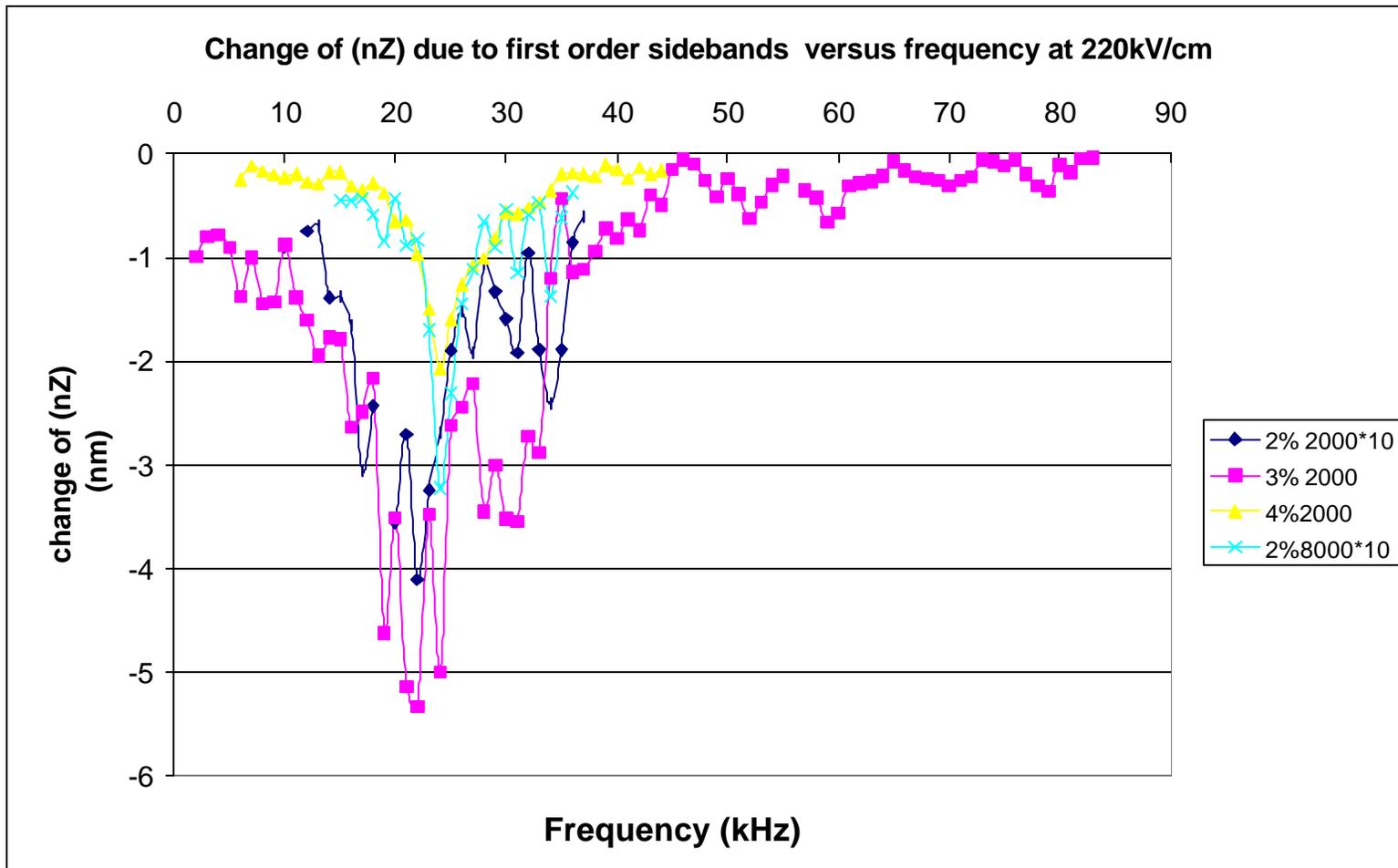


Figure 5.3 The change of (nZ) due to the first order sidebands versus frequency at 220kV/cm

- n is the refractive index of the film along applied electric field direction, d is the instantaneous film thickness as defined in section 5.1.
- *10 represents 10 times magnification.

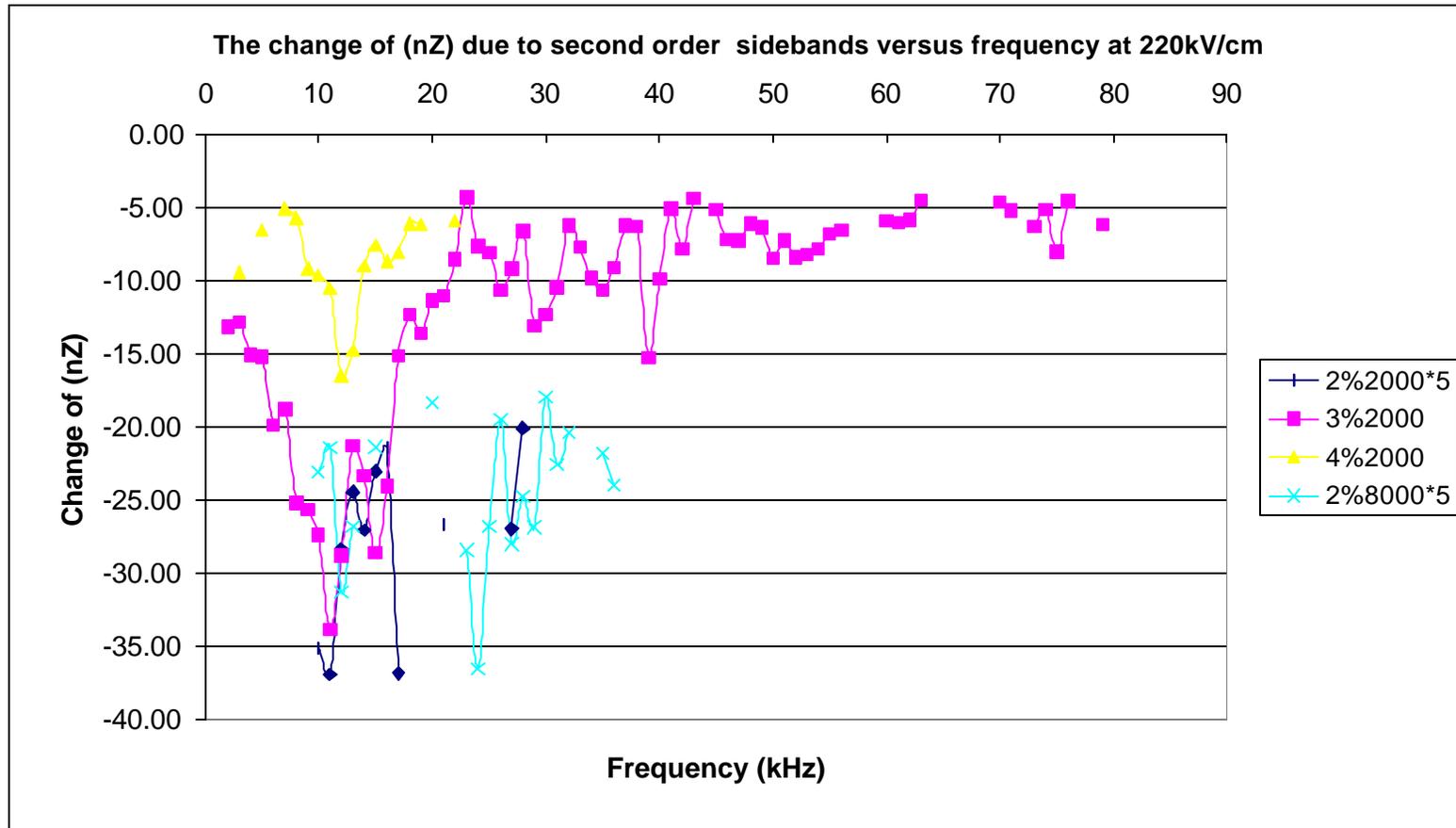


Figure 5.4 The change of (nZ) due to the second order sidebands versus frequency at 220kV

*5 represents 5 times magnification

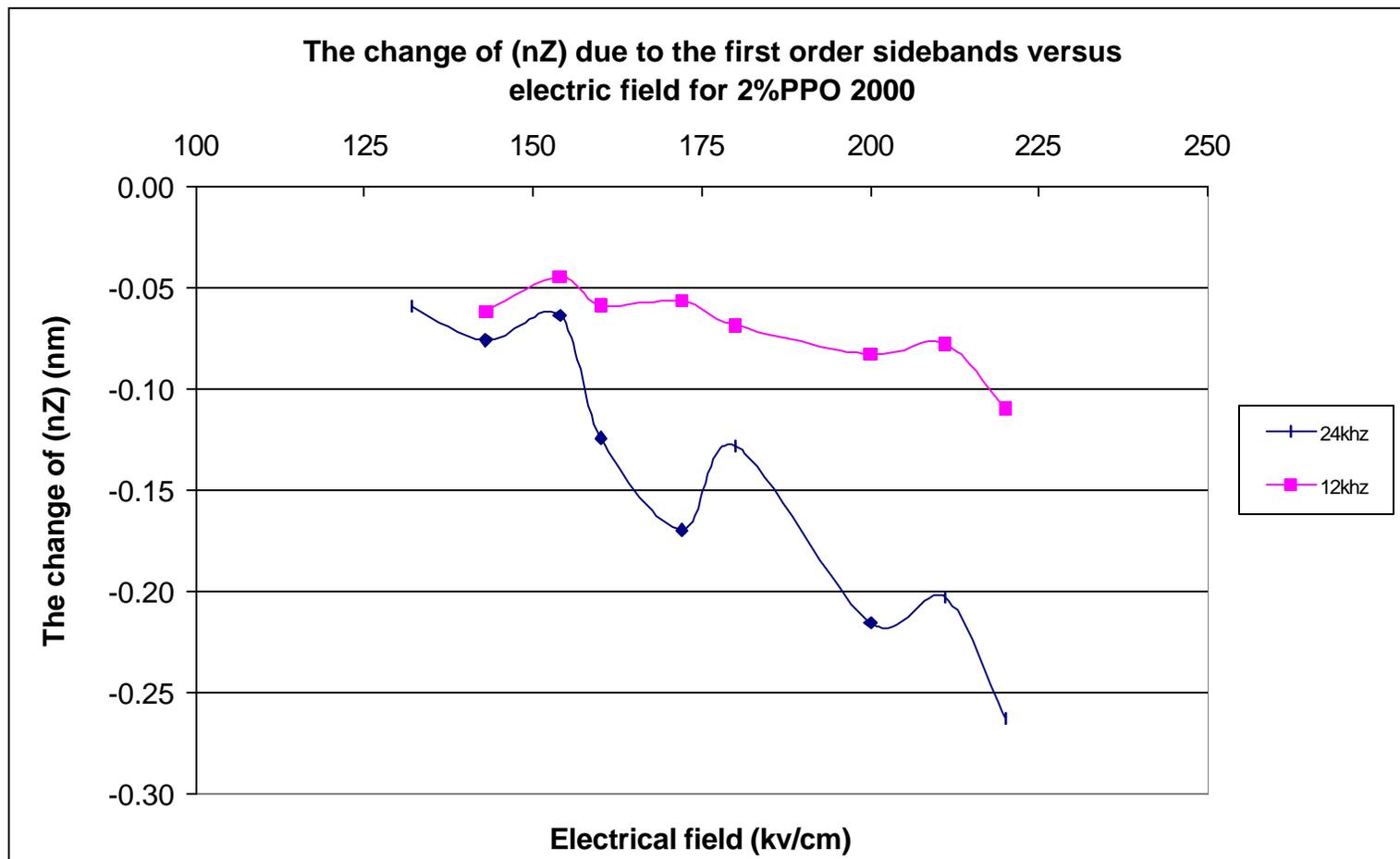


Figure 5.5 The change of (nZ) due to the first order sidebands versus electric field amplitude for 2%PPO 2000

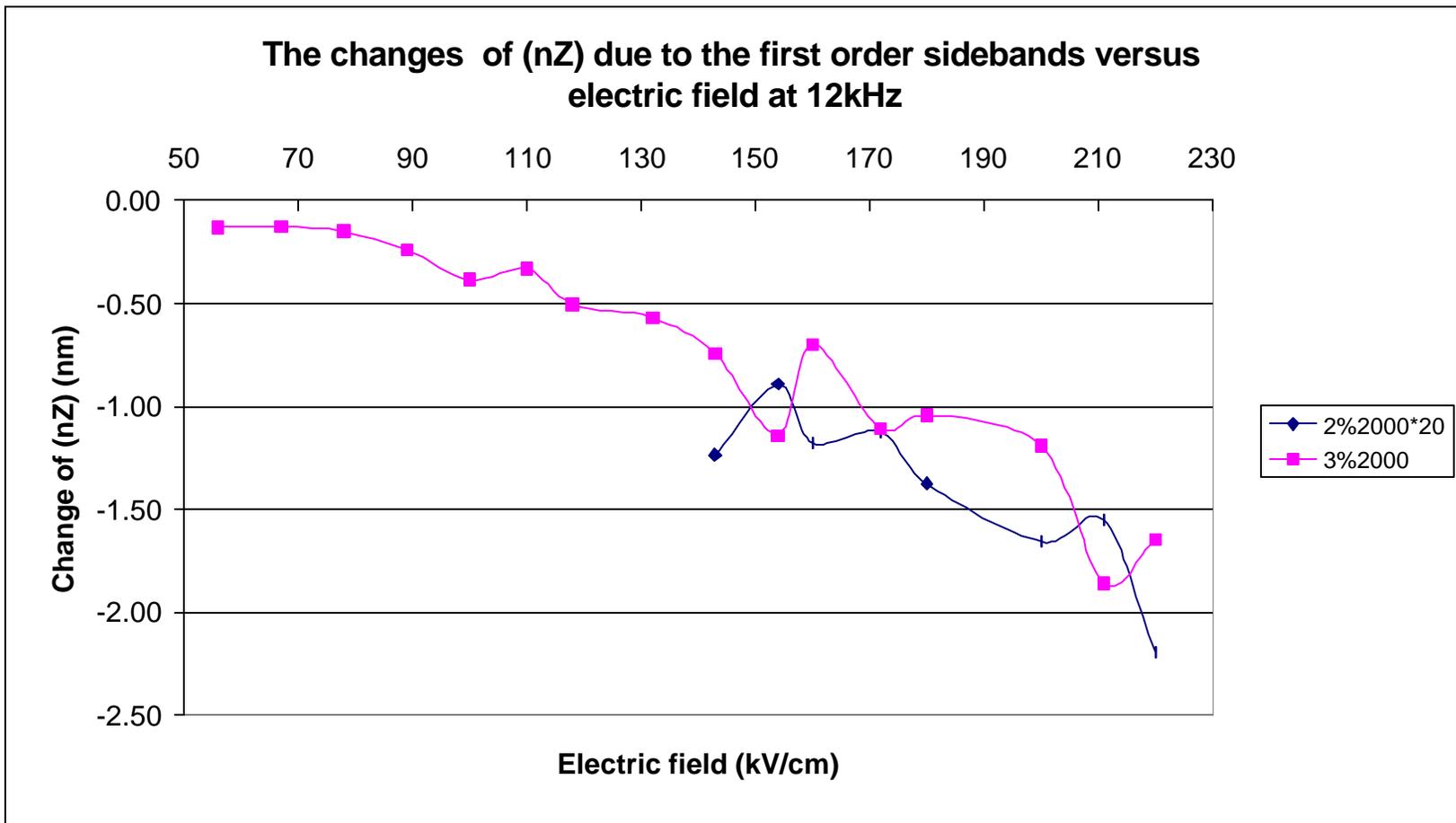


Figure 5.6 The change of (nZ) due to the first order sidebands versus electrical field at 12kHz.

*20 represents 20 times magnification.

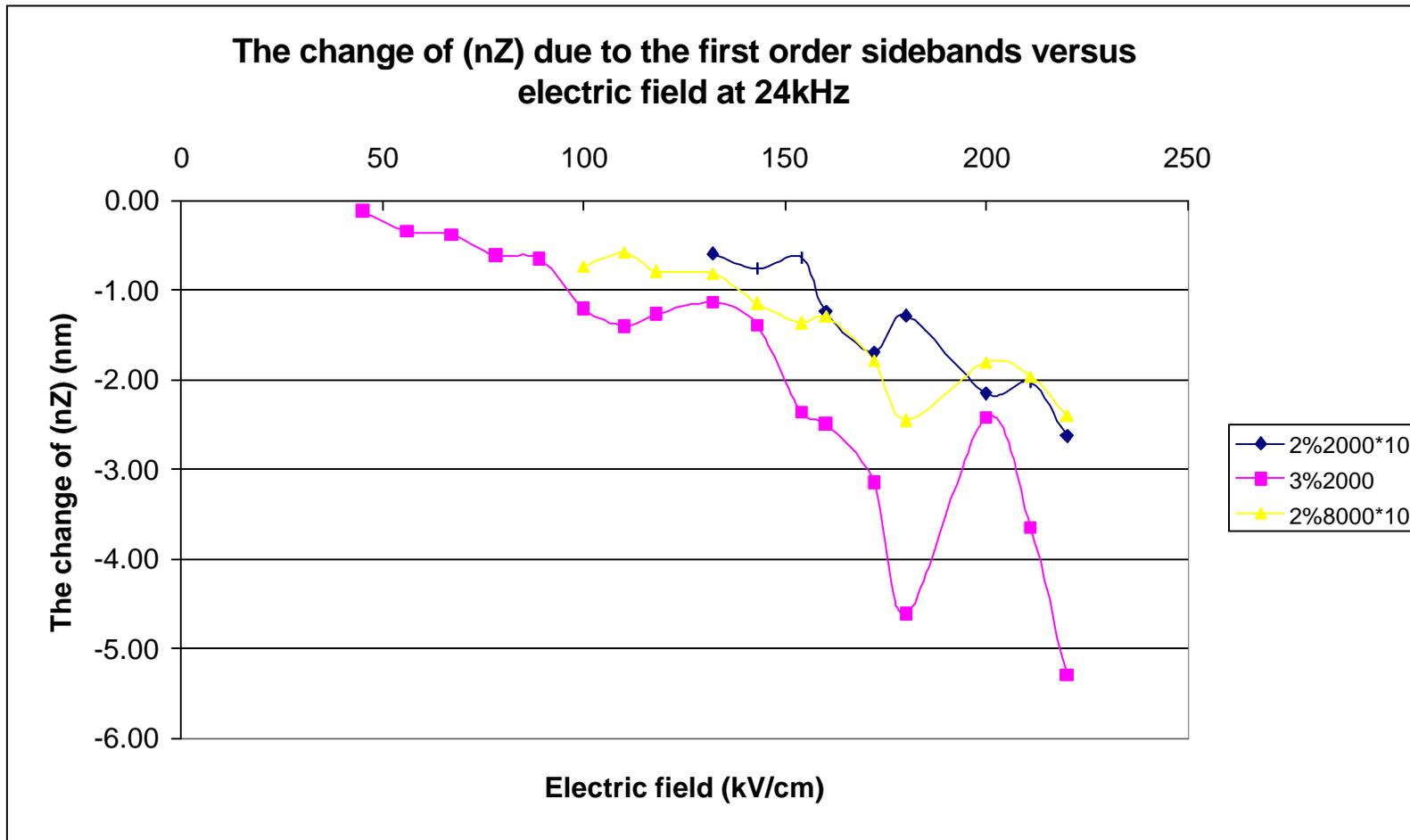


Figure 5.7 The changes of (nZ) due the first order sidebands versus electric field at 24kHz.

*10 means 10 times magnification.

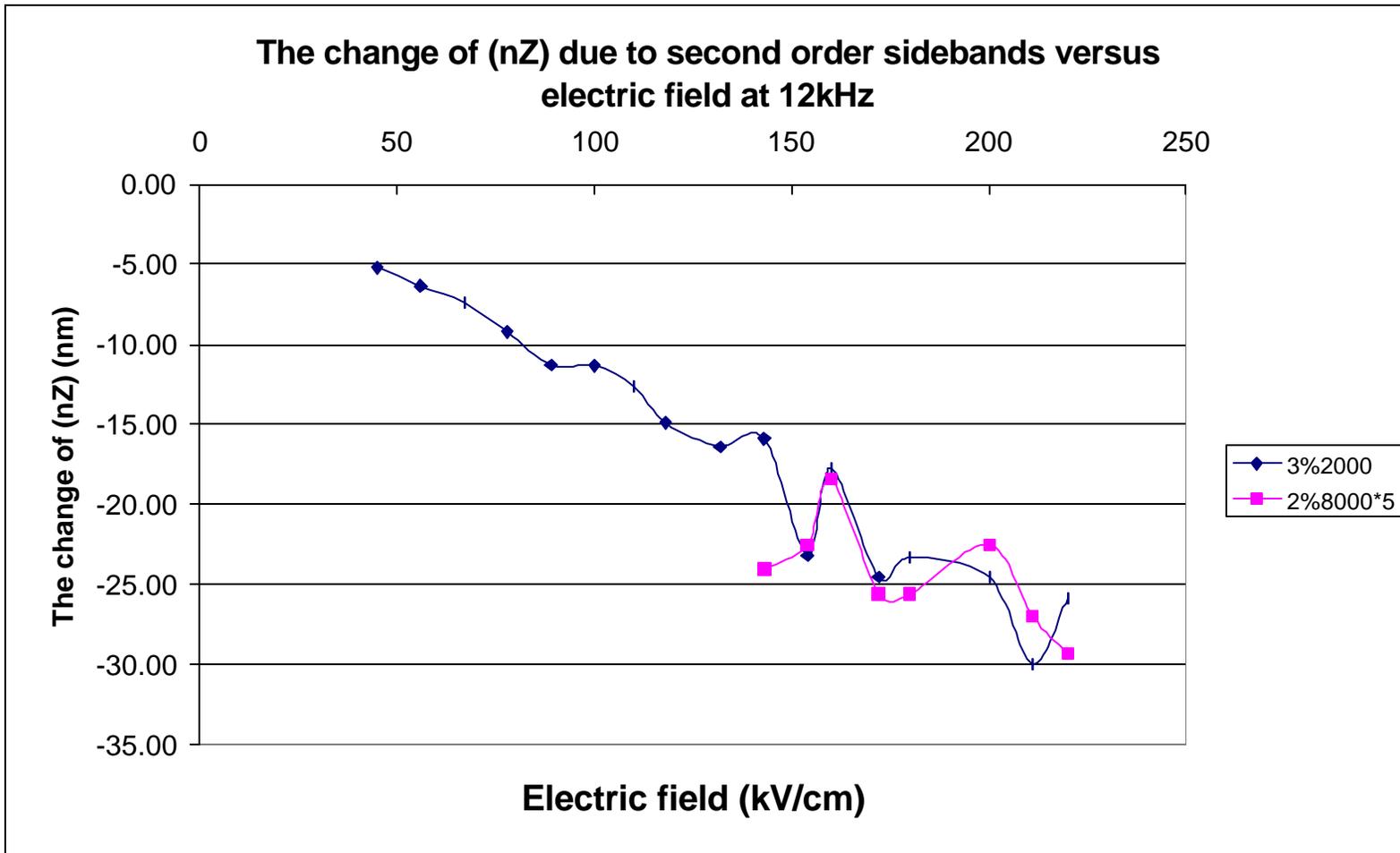


Figure 5.8 The changes of (nZ) to the second order sidebands versus electric field at 12kHz.

*5 means 5 times magnification

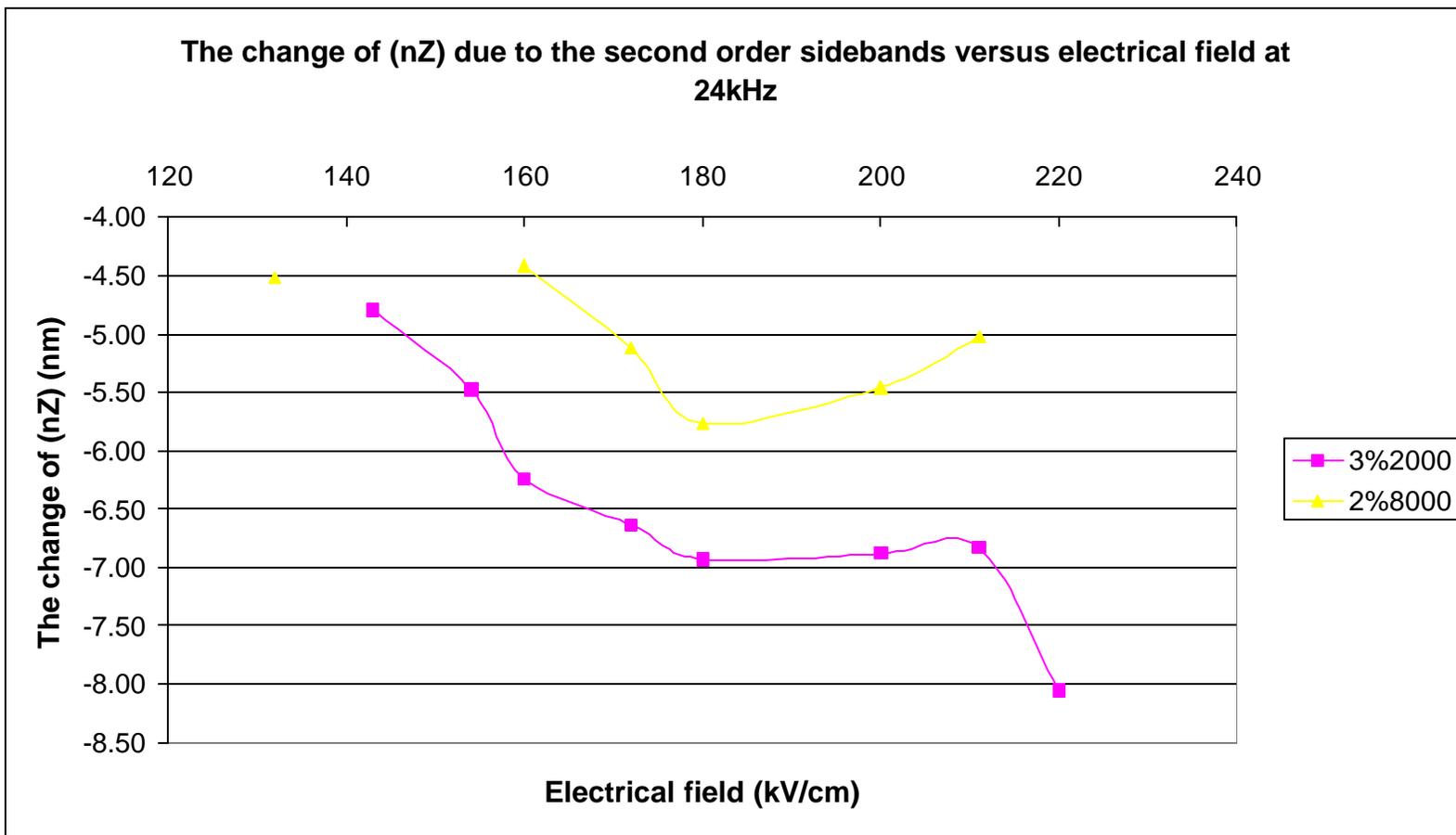


Figure 5.9 The change of (nZ) due to the second order sidebands versus electric field at 24kHz

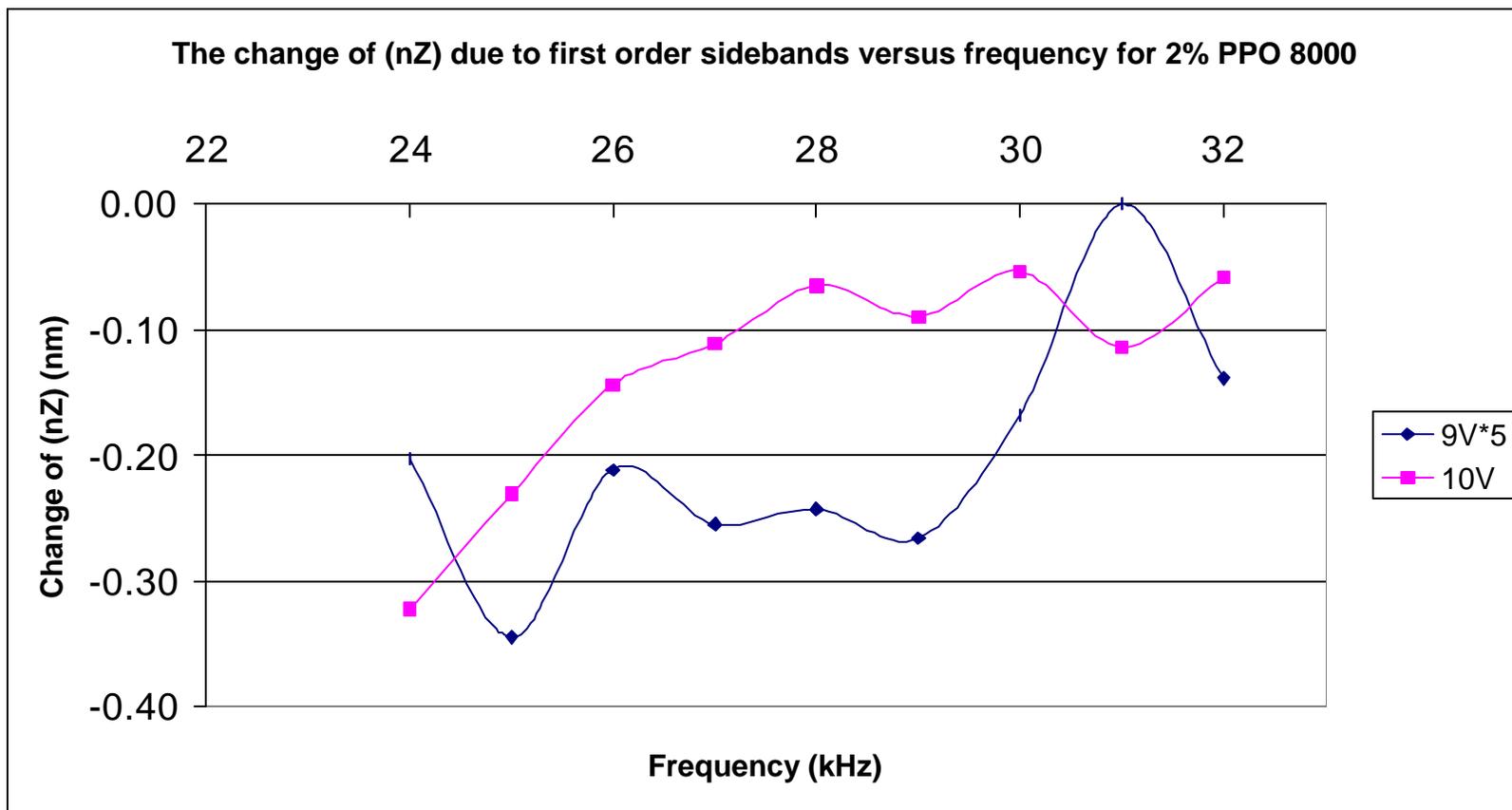


Figure 5.10 The change of (nZ) due to the first order sidebands versus frequency at different field strength

*9V equals to 200kV/cm field and the data series are magnified by 5 times.

10V equals to 220kV/cm field.

Table 5.3 Total refractive index times thickness change at 220kV/cm with and without polarizer

Mol. Wt.	Wt.%	AC frequency (kHz)	E field (kV/cm)	With or Without polarizer	Initial thickness (nm)	The change of (nZ) (nm)
8000	2%	12	220	Yes		-11.64
8000	2%	12	220	No	313	-23.17
8000	2%	24	220	Yes		-26.45
8000	2%	24	220	No	313	-26.07
2000	3%	12	220	Yes		-16.78
2000	3%	12	220	No	103	-15.60
2000	3%	24	220	Yes		-1.61
2000	3%	24	220	No	103	-1.65

Chapter 6 Conclusions and Future Work

6.1 Conclusions

A heterodyne interferometer was successfully built and utilized for investigating polymer chain dynamics under electric field. PPO thin films spin-cast on gold line samples were used in this thesis. Results show that strong electric field can induce nonlinearity in polymer films. Both electrorestrictive effect that is proportional to the square of electric field amplitude² and piezoelectric effect that is proportional to electric field amplitude² were observed. The effect of electric field strength, frequency, film thickness and polymer molecular weight on the electrical properties of PPO was studied.

Asymmetric polar polymeric materials can be poled under strong electric field and exhibit electro-optical properties such as piezoelectric and electrorestrictive effects. The magnitude of this nonlinearity in polymer films can provide detailed information about the structure of material. Polar groups orient along the electric field leading to birefringence along the field direction. In PPO, the refractive index of the film is larger in the field direction than in the perpendicular direction.

The interfacial effects affect polymer chain dynamics dramatically. Surface mobility arising from the film-air interface in ultra thin films is observed. The enhanced mobility in thin films enables us to measure polymer chain dynamics due to surface effect. Thinner PPO films respond to larger electric frequency ranges than thicker PPO films.

Substrate effect is also very important for polymer chain dynamics. The chemical bonding between the solid substrate and PPO molecules serves as an anchor for polymer chains under electric field. Without the substrate effect, PPO does not show any piezoelectric and electrorestrictive effects.

Polymer molecular weight affects polymer chain mobility and relaxation time dramatically. High molecular polymers have larger chain entanglements and intermolecular forces that result in their much slower response to electric field. Thus, the piezoelectric and electrorestrictive effects would be smaller in smaller molecular weight polymer films of the same thickness.

Finally, electric field strength and electric frequency affect polymer film thickness change and orientation. Higher intensity electric fields induce larger piezoelectric and

electrorestrictive effects in polymer films. Lower electric field intensity is required to overcome thermal agitation and intermolecular forces between polymer molecules to show long-range order of polymer chains. Electric frequency is equally important for polymer electro-optical effects. Polymers exhibit molecular resonance frequencies. At resonance frequency, polymers show the maximum electrical effects and also polymer molecules respond to electrical field stimuli in much shorter time and at much higher magnitude.¹² Electric field intensity will affect polymer local resonance frequency. The highest responding frequency of polymer molecules to electric field is limited by polymer chain slow dynamics and long relaxation time. We also observed that the piezoelectric effect of polymers happens at higher frequency than the polymer orientation. This result is due to the slow polymer chain dynamics and thus polymer chain cannot orient with high electric frequency.

6.2 Future work

6.2.1 Birefringence study of polymer films

Birefringence of polymer film under electric field can be further studied using this interferometer setup. In our current work, samples are placed parallel to the electric field of the laser beam that is parallel to the applied electric field shown in figure 6.1. Thus, we can measure the refractive index of the film along the applied electric field. When we turn the sample 90 degrees, the electric field of the laser beam is perpendicular to the applied electric field shown in figure 6.2, thus we measure the refractive index of the film perpendicular to the applied electric field in which polymer is not oriented. By comparing the data of the above two cases, we can measure the birefringence of polymer film. n_1 is the refractive index along applied field direction. n_2 is the refractive index of the film perpendicular to the applied field direction. $\Delta(n_1Z)$ is the changes of refractive index n_1 times instantaneous film thickness. $\Delta(n_2Z)$ is the changes of refractive index n_2 times instantaneous film thickness Z . ω is the applied electric field frequency.

6.2.2 Polymer film aging under external field

Dielectric materials subjected to high electrical field strength can produce highly reactive chemical species that contribute to the aging process of polymer dielectrics

films. This field has attracted significant attention in recent decade. Results of electrical aging will illustrate the basic mechanism that control the electron-dielectric interactions and provide a description of the basic degradation processes involved during the electronic aging.¹³ Polyethylene was already shown to have electrical aging under AC voltage due to the build-up of space charge.¹⁴ Polymer refractive index change under external field can be directly related to polymer aging. The current heterodyne interferometer can be used to study the online dynamics of polymer film electrical aging or thermal aging by adding a thermal-control heating stage and increasing the external field voltage.

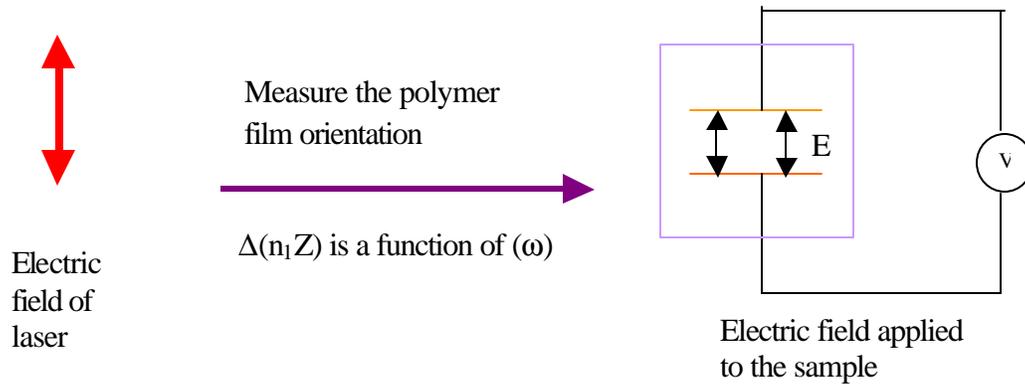


Figure 6.1 The electric field of the laser beam parallel to the applied electric field

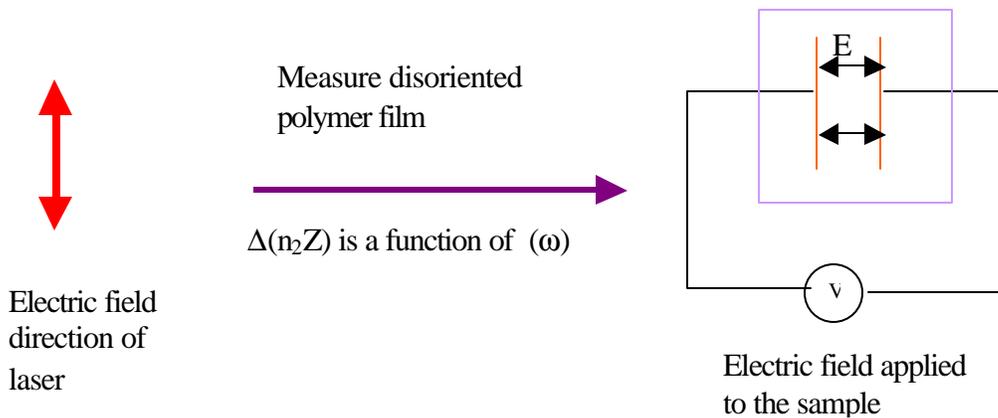


Figure 6.2 Electric field of the laser perpendicular to the applied electric field

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Vita

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