

STUDY ON THE POLING PROPERTIES OF NONLINEAR OPTICAL ACTIVE DERIVATIVE OF POLY (*p*-HYDROXYSTYRENE):(PS)O-DCV

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ABSTRACT

In this paper, the poling properties of (PS)O-DCV, a derivative of poly (*p*-hydroxystyrene), was reported. The investigations showed that the thermochromism correction, which was neglected in the literatures, should be considered in the measurements of order parameter of poled films with electrochromism technique. Here, another linear optical method, IR and polarized IR spectra for characterizing of poled films was suggested first time. The bulk second nonlinear optical coefficient d_{33} of poled films could be estimated by measured order parameter semi-qualitatively.

INTRODUCTION

The importance and development of optoelectronics have brought about a great advance in the research of the nonlinear optical (NLO) polymeric materials. It is well known, one of the essential conditions for a useful second order NLO material is to create a noncentrosymmetric molecular assembly having high structural order and suitable processability. One of approaches is to incorporate organic NLO active molecules possessing large second order susceptibility β into amorphous polymer, poling with an external field at elevated temperature, removing the field when cooled down to room temperature. It is called poled polymer. In this sort of material, the residual molecular orientation allows them to exhibit second order nonlinear optical properties. Since the 1980s, the research on the poled polymer had been made a marked progress.

So far two forms of second order NLO polymers have been studied; transparent amorphous polymers doped with NLO molecules, i. e., host/guest system and polymers covalently functionalized with NLO chromophores. To develop an usable poled polymeric film several problems must be solved: raising the macroscopic second order NLO coefficient d_{33} , extending the stability of orientation and reducing absorption coefficient of films. Since covalently functionalized NLO polymers have many advantages over host/guest system, such as higher number density of NLO moieties and much improved stability of orientation, enabling us to solve the above-mentioned problems, so the covalently functionalized NLO polymers are developing quickly.

A popular and direct approach to measure d_{33} of poled film is the Maker fringe technique^[1]. However, it requires expensive YAG laser source and optical testing system and complicated calculations. Recently, various methods to estimate d_{33} value by measuring order degree with conventional linear optical techniques had been suggested. For example, Mortazavi et al. demonstrated the orientation of

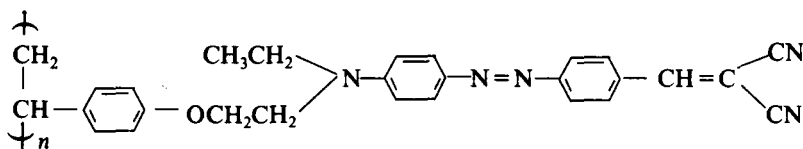
poled films could be determined by UV-Visible absorption spectra measured before and after poling^[2]. Later, a theoretical analysis of the method was established by Page et al^[3]. They pointed out this method could be used to measure the order degree of poled film and estimate the poling field. Since the interpretation is direct and conclusive, UV-Visible spectrum method has been adopted by more and more laboratories. In the same paper, the optical waveguiding technique, which could be used to measure small changes in the refractive index anisotropy, was demonstrated to be a sensitive means to monitor the poling-induced order and its relaxation. However, complicated optical waveguiding techniques had limited its application.

Infrared dichroism is one of powerful tool for studying orientation in polymer^[4]. In this paper the order degree of poled films of (PS)O-DCV was measured by IR and polarized IR spectra as well UV-Visible spectra techniques. The IR method was first time used to characterize the order degree of poled films. The experiments showed that the method can not only observe the poled degree of films, but also estimate the d_{33} value of films through measuring dichroic ratio R . Its results coincided with UV-Visible absorption spectrum method well.

EXPERIMENTAL

1. Film preparation and poling

The films were prepared as follows. A solution of synthesized copolymer of p-2-[N-ethyl-N-(4'-dicyanovinyl) azobenzene] aminoethyloxy styrene with poly(*p*-hydroxystyrene), (PS)O-DCV^[5], in 1, 2-dichloroethane was spun coated onto a transparent microscope slide or a KBr crystal plate. The former was used for UV-Visible absorption spectra measurements, its thickness was controlled with the absorbance of charge transfer band absorption peak in the range of 1 — 1.3 (about 1 — 3 μm from interference microscope). The latter was used for IR measurements, to obtain a good spectrum the typical thickness was about 10 μm . The prepared films were dried in vacuum at about 60 °C for over two hours, then at 100 °C for over 6 hours to remove residual solvent. The dried films were poled with the poling apparatus described previously^[6].



2. Measurements of spectra

The visible absorption spectra of the films were measured with a JA SCD UVIDEK-320 UV-Visible spectrophotometer (made in Japan). The IR and polarized IR spectra of the films were measured with PE 983 Infrared spectrophotometer. To measure infrared dichroism the film was fitted on the frame which has 45 ° inclination with respect to incident IR beam.

RESULTS AND DISCUSSIONS

1. UV-Visible absorption spectra

Figure 1 showed the typical UV-Visible absorption spectra of unpoled and poled (PS)O-DCV films. The selected poling conditions were as follows. The poling voltage was 10 KV, poling temperature was 117 °C (T_g of synthesized (PS)O-DCV was 106 °C , measured with DuPont Delta ser DSC 7 calorimetry) and poling time was 15.33 hours. The experiments showed the absorbance of the charge transfer band of film was decreased obviously after poling. The observed reduction of absorbance was not only caused by external field, it also could be observed merely at heating (curve 2 in Fig. 1). The latter phenomenon has not been described in the literatures yet. The elemental analysis and IR spectra measurements showed there were no chemical change and the peak position of UV-Visible spectra of film was almost not shifted during heating or poling, therefore, the observed thermochromism may be caused by the change of condensation state of the polymer films. So thermochromism correction must be introduced to calculate the orientation of poled films with the formula^[2, 3]

$$\Phi = 1 - \frac{A_{\perp}}{A_0} \quad (1)$$

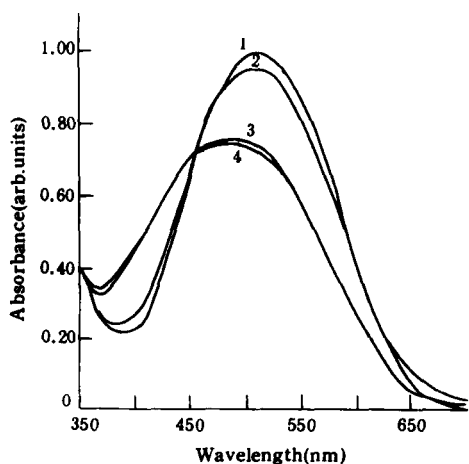


Fig. 1 The UV-Visible absorption spectra of unpoled and poled (PS)O-DCV films
1. unpoled; 2. heating (without field)
3. after poling; 4. three days after poling
Poling conditions: 117 °C , 10KV, 15.33 h

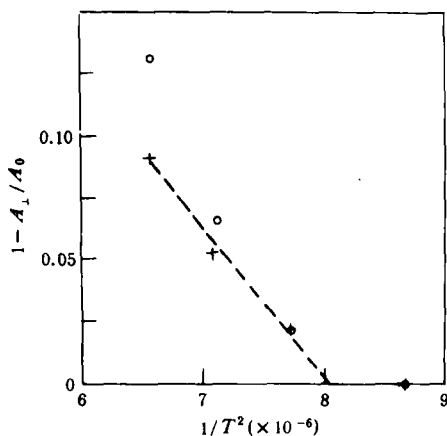


Fig. 2 The dependence of order parameter Φ of poled (PS)O-DCV films on poling temperature.
(○) experimental; (+) after thermal correction
Poling conditions: 10KV, 6h.

The poling of (PS)O-DCV films were performed at different temperatures, voltages and times. Based on the poling principle, the poling efficiency is determined by the potential energy of the molecular dipoles in the applied field relative to the energy associated with thermal fluctuations of the system, that is:

$$U = \frac{\mu E_p}{kT} \quad (2)$$

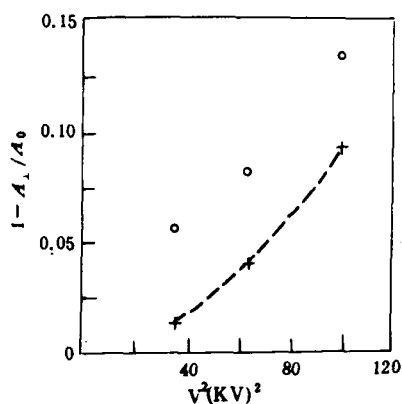


Fig. 3 The dependence of order parameter Φ of poled (PS)O-DCV films on poling voltage (O) experimental; (+) after thermal correction
Poling conditions: 177 °C, 6h.

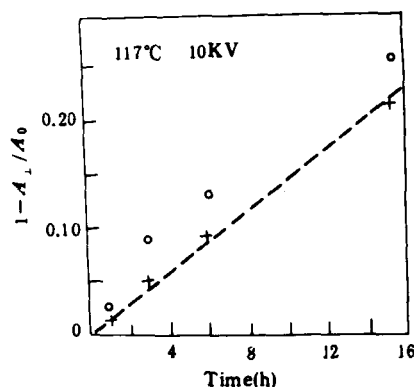


Fig. 4 The dependence of order parameter Φ of poled (PS)O-DCV film on poling time (O) experimental; (+) after thermal correction
Poling conditions: 10KV, 117 °C

However, there are two states: orientation alignning (high temperature) state and orientation freezing (room temperature) state in the COPET procedure. The permanent dipoles of the polymer experience a force tending to align them in the direction of the field at the high temperature. Then, the new alignment of the film is freezed at room temperature. These two states both are thermodynamic equilibrium state, their poling efficiency can be written as $\frac{\mu E_p}{kT_p}$ and $\frac{\mu E_p}{kT_r}$ (T_p is the poling temperature, T_r is room temperature), respectively. The measured net orientation will be determined by the difference of them. Following the Page's analysis^[3],

for $U \leq 1$

$$\Phi \approx \frac{U^2}{15} \quad (3)$$

that is

$$\Phi \approx \frac{1}{15} \left(\frac{\mu E_p}{k} \right)^2 \left(\frac{1}{T_r^2} - \frac{1}{T_p^2} \right) \quad (4)$$

From formula (4), the large order parameter Φ will be achieved at higher poling temperature. The experiments showed that the Φ values of poled films after thermochromism correction exhibit a good linear dependence on T_p^{-2} at the temperature range from 360K to 390 K (Fig. 2). It was in agreement with above formula (4). In (PS)O-DCV the orientable chromophore was attached to the backbone as side chain of polymer, the phase transition temperature for orientation would be T_β . In general, T_β is lower than T_g about 20 — 30 °C. Therefore, the deviation from linear dependence at lower than 80 °C can be understood. This observed deviation coincided with our previous work^[7]. It is worthy of notice that the structural change had been observed at higher temperature

(such as 147 °C) poling. Fig. 3 showed the change of Φ as poling at different voltages. The $\Phi - V^2$ relationship was not linear. It may be related to complicated corona poling procedure. The corona poling field depends on the electrode configuration, the $E_p - V_p$ relationship becomes complicated and is not linear in the cases. The alignment of chromophore units for used side chain covalently functionalized copolymer system will be more difficult since the main chain of polymer must be

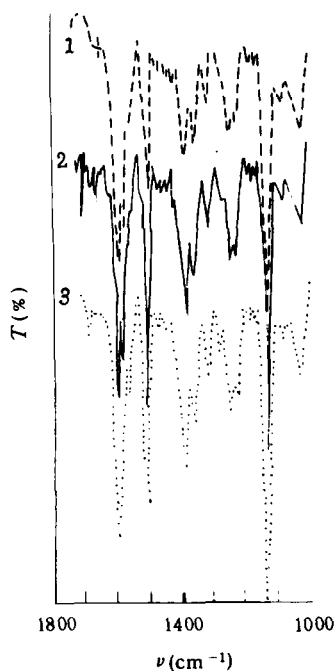


Fig. 5 The IR spectra of unpoled and

poled (PS)O-DCV films

1. unpoled; 2. after poling;

3. poled; IR irradiation for a long time

turned in order to align the chromophore side groups. This procedure experiences a high viscosity. So that, to achieve thermodynamic equilibrium will take longer poling period. Fig. 4 gave the Φ dependence on the poling time, a good $\Phi - t$ linear relation can be seen. The saturation poling had not been arrived even after 15.33 hours.

After thermochromism correction, the order parameter of (PS)O-DCV films at 117 °C, 10KV and poled for 15.33 hours with disktop electrode configuration was $\Phi = 0.21$, it was very close to the results of parallel wire electrode configuration corona onset poling at elevated temperature ($\Phi = 0.23$)^[2].

2. IR spectra

The position of absorption bands of IR spectrum are determined by molecular structure and the absorption

intensities are obviously changed at different measuring states. Though poling had not led to chemical structural change, the chromophore was oriented partly and some changes of charge distribution in molecules occurred. This change could be utilized to investigate the poling process of films qualitatively. The experiments showed, the IR absorption bands of poled films were similar to that of unpoled films, but several peak intensities changed obviously. Fig. 5 indicated the changes in the range between 1000 and 1800 cm^{-1} . The absorption intensities of phenyl ring stretching vibration bands at 1597, 1582, 1507 and 852 cm^{-1} were increased after poling and the intensity of vibration band at 1242 cm^{-1} , which belongs to ether bond linked to phenyl ring, was increased, too. These indicated the parallel component of phenyl ring with incident radiation beam was increased after poling, i. e., the phenyl ring was aligned perpendicular to the substrate. It was in agreement with the direction of poling field.

It is worth noticing that the absorption of 1507 cm^{-1} increased remarkably after poling. Its height was even higher than that of 1582 cm^{-1} , but the 1507 cm^{-1}

absorption was weaker than that of 1582 cm^{-1} in the unpoled films. Moreover, the height of 1507 cm^{-1} peak was decreased with the film exposed in IR radiation for a long time due to the relaxation of orientation, the 1507 cm^{-1} absorption was weakened again than that of 1582 cm^{-1} . It may be related to the relative orientations of the symmetric or asymmetric stretching vibration modes. So the relative change between 1507 and 1582 cm^{-1} can be used to study the poling and relaxing processes qualitatively.

3. Infrared dichroism

As well known, the IR absorption intensity of a vibration can be written as:

$$A \sim (\langle M \cdot E \rangle)^2 = K \cdot \cos^2 \alpha \quad (5)$$

where A is the absorbance, α is the angle between transition dipole moment vector M and electric vector of incident radiation E , and K is a constant independent of orientation. If E is parallel to M , A is a maximum. If E is perpendicular to M , A is a minimum. The absorbance measured is an average over all orientations of the particular vibration in the polymer sample. Thus, the orientation of polymer films can be determined by the dichroic ratio R . It is defined by

$$R = A_{\parallel} / A_{\perp} \quad (6)$$

R can be related to the Hermans orientation function Φ ^[8]

$$\Phi = \frac{R-1}{R+2} \cdot \frac{2}{3\cos^2\beta-1} \quad (7)$$

where β is the angle between the dipole moment vector and the chain axis, thus Φ value can be obtained by measured R .

Table 1 listed the measured $A_{\perp}$ and $A_{\parallel}$ of unpoled and poled (PS)O-DCV films (poling at: 10 KV, 117°C and 7 hours). The experiments showed the dichroic ratio of unpoled films was $R \approx 1.00 \pm 0.02$, this means the instrument error was about 0.02. From Table 1 the R was around 1.1 for most of vibrations, it indicated the films had been oriented partly after poling. Based on the chromophore molecular structure a vibration band of phenyl ring was chosen for calculation of orientation function, i. e., $R = 1.14$.

According to the formula (7), the angle β must be known for calculating Φ value accurately. However, the value of $2/(3\cos^2\beta-1)$ is larger than 1, and it can be assumed that the angle β was affected by different poling conditions slightly due to rigid molecular chromophore. Thus, the minimum Φ can be calculated by measured R value, that is:

$$\Phi_{\min} = \frac{R-1}{R+2} \quad (8)$$

From data listed in Table 1, $\Phi_{\min} \approx 0.045$ based on the UV-Visible spectra measurements (Fig. 4), the corrected Φ value was about 0.1 at the same poling conditions. These results were quite close with each other.

The angle β can be determined by several other techniques or mathematical fit method. The work is in progress.

4. The estimation of d_{33} values of poled films

Based on the oriented gas model of poled films^[9], d_{33} value can be described

as follows :

$$d_{33} = \frac{1}{2} \cdot N \cdot \beta \cdot f^{2\omega} \cdot (f^{\omega})^2 \cdot \langle \cos^3\theta \rangle$$

(9)

where N is the number density of chromophore in poled films, β is molecular hyperpolaribility, f is Lorentz local field factor and 2ω and ω represent doubling frequency and fundamental frequency, respectively. These parameters are constants for a type of polymer system, $\langle \cos^3\theta \rangle$ is the sole variable parameter, θ is the angle between dipole moment vector and poling field, it can be obtained by an order parameter (orientation function)^[2, 10, 11]:

$$\Phi = \frac{1}{2} (3 \langle \cos^2\theta \rangle - 1)$$

(10)

Table 1 Infrared dichroism of poled (PS)O-DCV films

ν (cm ⁻¹)	Unpoled	Poled		ΔA	R	Vibration mode
	$A_{ }^u$	$A_{ }^p$	$A_{\perp}^p$	$A_{ }^p - A_{ }^u$	$A_{ } : A_{\perp}$	
2927	0.091	0.105	0.100	0.01	1.05	ν (CH ₂)
2229	0.086	0.094	0.081	0.01	1.16	ν (CN)
1597	0.358	0.419	0.371	0.06	1.13	ν (Ar)
1582	0.299	0.320	0.290	0.02	1.10	ν (Ar)
1561	0.127	0.133	0.118	0.01	1.13	ν (C=C)
1507	0.284	0.338	0.308	0.04	1.10	ν (Ar)
1383	0.199	0.216	0.195	0.02	1.11	ν (CH ₂)
1353	0.173	0.200	0.176	0.03	1.14	δ (O—H(Ar))
1308	0.102	0.118	0.105	0.02	1.12	δ (C—H)
1242	0.162	0.203	0.180	0.04	1.13	ν (Ar—O)
1220	0.127	0.150	0.135	0.02	1.11	ν (N—C)
1130	0.464	0.463	0.425	0.00	1.09	ν (O—CH ₂)
825	0.127	0.153	0.148	0.03	1.01	δ (Ar—H)
747	0.055	0.068	0.060	0.01	1.13	δ (C—H)

Table 2 The estimation of d_{33} of poled films

Polymer	N ($\times 10^{20}$ unit (cm ⁻³))	d_{33} ($\times 10^{-9}$ esu)			Ref.
		UV—Vis	IR	expt.	
(PS)O $\times$ DCV	14	320	290		This work
DR1—P MMA	2.74	22.8		20	[2, 12]
PPNA	40.6	48.3—103.6		74	[3, 13]
MNPAMS	28.5	86		67	[14]

The d_{33} value of poled (PS)O-DCV films had been estimated and the results were listed in Table 2. For checking the reliability of above inference, the SHG experimental results adopted from references [2, 12], [3, 13] and [14] and calculated results by formula (10) and (9) were listed in Table 2, too. The data showed that the calculation is reasonable and the results obtained from UV-Visible absorption spectra and infrared dichroism were quite close. Since the reported order parameter of poled films were the range between 0.05 and 0.3, in other words, $0.22 < \langle \cos^3\theta \rangle < 0.39$, so that the estimated d_{33} values were reliable in the order of magnitudes.

SUMMARY

In this paper a simple and practical linear optical technique to estimate the d_{33} value of poled films had been suggested. The order parameter of poled films was measured by infrared dichroism, then the d_{33} value could be estimated based on the oriented gas model of poled polymer films. The results were close to that from electrochromism. The method reliability had been demonstrated by comparison with the references. The method is direct and semi-quantitative. In addition, it had been found that the infrared spectra technique can be used to investigate the poling and its relaxation process of polymer qualitatively, too.

As reported, UV-Visible absorption spectra can be used to measure the order parameter of poled films and estimate the poling field E_p and investigate the relaxation of film's orientation. However, it has been found in this work that there exists the thermochromism, the correction must be considered to measure order parameter accurately.

The limitation of suggested IR method is the polarity and number density N of chromophore in the films. If the polarity of chromophore is too strong and N is too high, the centrosymmetric aggregates will be formed easily and they will not contribute to the d_{33} value. If the N is too low, the sensitivity of IR spectrophotometer will not be accurate enough to be measured. Even though its application range is limited, it is still a useful semi-qualitative method for characterization of most covalently functionalized NLO polymer in common chemical laboratory.

Keywords:

Nonlinear optical polymer; poling; electrochromism; IR dichroism; Order parameter

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