

THE EFFECT OF PHOTO-CROSSLINKING ON THE ORIENTATION STABILITY OF POLYVINYL ALCOHOL CONTAINING 4-NITRO-4'-ALKOXYSTILBENE AND CINNAMYL PENDENT GROUPS*

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ABSTRACT

Crosslinking is one of the effective routes for improving the orientation stability of poled polymer films. The derivative of polyvinyl alcohol containing 4-nitro-4'-alkoxystilbene and photo-crosslinkable cinnamyl groups as side chains has been synthesized. The in-situ simultaneous photo-crosslinking poling of synthesized polymer films has been performed. The second order nonlinear optical coefficient d_{33} of poled film is 11 pm/V. The SHG measurements show that the break-over temperature of SHG signal is raised obviously after irradiation, its orientation stability is doubled as compared with that of non-crosslinking samples.

INTRODUCTION

One of the key goals in the pursuit of device-applicable poled second-order polymeric nonlinear optical (NLO) materials is the temporal stability of poling-imposed chromophore/matrix acentricity, which presents a significant challenge in the material design. In order to prevent relaxation of the chromophores after poling, polymers with chemically crosslinked systems have been investigated. A much more stable alignment can be achieved in chemically crosslinked networks. For example, a thermally crosslinkable mixture of multifunctional epoxy monomers and nitrophenylamine chromophores shows good long term stability^[1,2]. The film thickness and the

* This work was supported by the National Natural Science Foundation of China

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Received January 16, 1996

crosslinking reaction are usually more difficult to adjust and to control if a low molar mass monomer mixture is used. Therefore several photo-crosslinkable NLO polymers have been studied^[3-5]. In these examples, the corona poling was carried out prior to the photocrosslinking reaction, the poling-induced alignment of chromophore may be destroyed partially during crosslinking. To improve the efficiency of poling we explore the in-situ simultaneous photo-crosslinking poling of chromophore-functionalized NLO polymer films containing additional photo-crosslinkable side chain. The approach presented here uses the copolymer of polyvinylcinnamate (PVCn), which can be crosslinked by UV-irradiation, and NLO active poly [vinyl-(4'-nitrostilbene-4-oxy) acetate] (PVNSOA) (Fig. 1, IV). The design of this system was initiated by a few promises. We expected that the synthesized polymer can undergo a crosslinking reaction without affecting the optical quality of the final rigid structure. Furthermore, the chromophore number density can be adjusted by changing the molar ratio of vinyl cinnamate with NLO chromophore pendant group. It can be poled and photocrosslinked simultaneously to yield a material with good optical quality, large second order nonlinearity and improving temporal orientation stability.

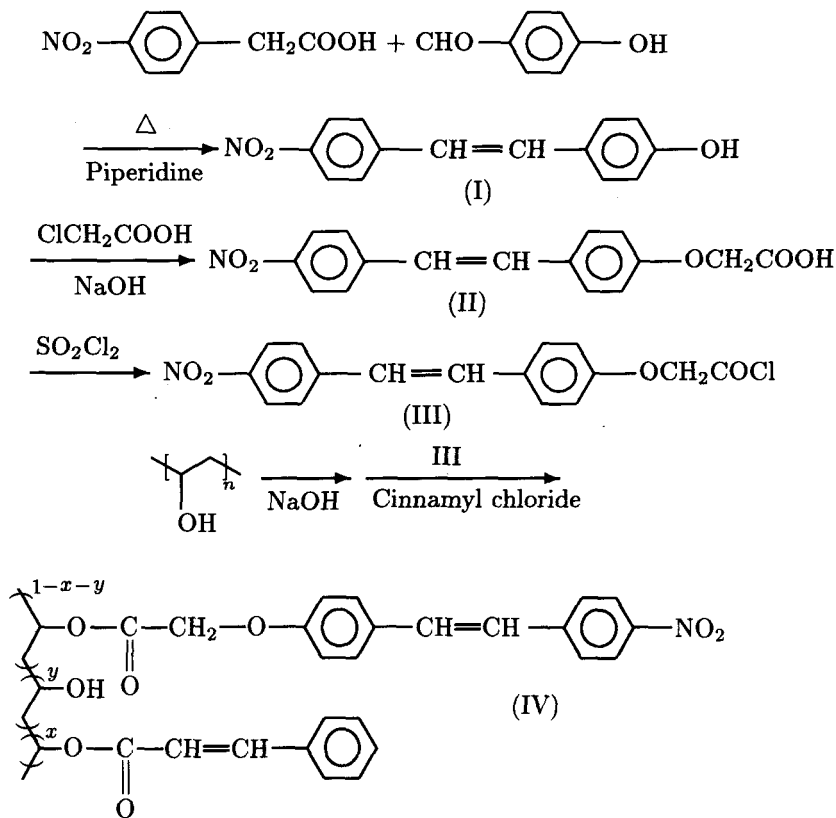


Fig. 1 Structure and synthesis of title copolymer

EXPERIMENTAL

1. *Synthesis of polymer*

Chemically pure polyvinyl alcohol, p-nitrophenylacetic acid, chloroacetic acid, p-hydroxybenzaldehyde and piperidine etc. were purchased from Beijing Chemical without further purification. Cinnamyl chloride, sulfonyl chloride and the solvents dimethyl sulfoxide (DMSO), dichloroethane, pyridine were redistilled before use.

^1H NMR and FT-IR spectral data were obtained on a Varian Unity 200 MHz NMR spectrometer and Bruker model IFS-113 spectrometer, respectively. Elemental analyses were carried out by Heraeus CHN-Rapid method. Melting points were determined on a X-4 micro-melting-point apparatus without correction. The phase transition temperature T_g of polymer was determined by using a SR-1C differential scanning calorimeter with a heating rate of $20^\circ\text{C}/\text{min}$.

(1) 4'-Nitro-4-hydroxystilbene (I)

5 g p-hydroxybenzaldehyde (41 mmol), 7.4 g p-nitrophenylacetic acid (41 mmol) and 3.5 g piperidine (41 mmol) were mixed in a round-bottom flask equipped with reflux condenser and magnetic stirrer. The mixture was heated in an oil bath at 115°C , and a large amount of gas was evolved at beginning. After about 2.5 hours the reacting mixture changed to an uniform liquid. Then, the temperature of the oil bath was raised to 140°C and the reaction was continued for another 5 hours. The formed red solid was dissolved in acetone and neutralized with dilute HCl aqueous solution, then it was poured into water. The precipitate was collected with filtration and dried in vacuum. Yield 6.9 g (69.8%). mp. $212\text{--}214^\circ\text{C}$.

$\text{C}_{14}\text{H}_{11}\text{O}_3\text{N}$	Calc.	C 69.69%	H 4.59%	N 5.80%
	Found	70.19%	4.67%	5.71%

^1H NMR (DMSO- d_6 , ppm): 6.80 (d, 2H, $J=8.8\text{Hz}$), 7.16 (d, 1H, $J=16\text{Hz}$), 7.38 (d, 1H, $J=16\text{Hz}$), 7.49 (d, 2H, $J=8.6\text{Hz}$), 7.77 (d, 2H, $J=9.0\text{Hz}$), 8.17 (d, 2H, $J=8.8\text{Hz}$), 9.75 (br., 1H).

(2) 4'-Nitrostilbene-4-oxyacetic acid (II)

In a round-bottom flask equipped with condenser and magnetic stirrer, 4 g 4'-nitro-4-hydroxystilbene (I, 16.6 mmol) and 20 ml DMSO as solvent were added and heated at 80°C in an oil bath until the solution was formed. Then, a solution of 1.6 g chloroacetic acid (17 mmol) and 1.3 g NaOH (33 mmol) in 7 ml H_2O was added dropwise. The mixture was reacted for 4 hours under stirring and heating at 100°C and it was diluted with 10 ml H_2O and 10 ml DMSO. Thereafter, the solution of 0.8 g NaOH and 0.8 g chloroacetic acid in 10 ml DMSO and 5 ml H_2O was added and

reacted for another 6 hours. The system was acidified with diluted HCl aqueous solution to pH 3 and poured into water to precipitate the yellow material. The solid was collected with filtration and dried in vacuum. It was recrystallized with ethanol. Yield 3.0 g (60%). mp. 223—226°C.

$C_{16}H_{13}NO_5$	Calc.	C 64.21%	H 4.38%	N 4.48%
	Found	64.31%	4.68%	4.74%

(3) 4'-Nitrostilbene-4-oxyacetyl chloride (III)

4.9 g 4'-Nitrostilbene-4-oxyacetic acid (II, 16.4 mmol), 40 ml petroleum ether (b.p. 60—90°C) and 20 ml sulfonyl chloride were added to a round-bottom flask equipped with magnetic stirrer and condenser, which was connected with $CaCl_2$ dry tube and bubble counter. Under stirring the uniform solution was formed, then it was heated in an oil bath at 75°C and gas bubbles appeared. The reaction was continued for 7 hours, then petroleum ether and excess sulfonyl chloride were removed under reduced pressure. 4.4 g raw product was obtained and it can be used without purification.

$C_{16}H_{12}NO_4Cl$	Calc.	C 60.48%	H 3.81%	N 4.41%	Cl 11.15%
	Found	59.81%	3.87%	4.22%	10.67%

(4) Title copolymer (IV)

0.44 g polyvinyl alcohol and 11 ml redistilled fresh pyridine were placed into a flask and heated at 100°C for 12 hours to form the solution. After cooling 1.6 g 4'-nitrostilbene-4-oxyacetyl chloride (III, 5 mmol) in 25 ml dichloroethane was added and stirred overnight, then heated at 80°C for 2 hours. The system was cooled down to 55°C, 1.05 g cinnamyl chloride (6.3 mmol) was added and reacted at 55°C for another 5 hours. After cooling down to room temperature the reaction mixture was poured into very dilute H_2SO_4 solution to precipitate the copolymer. It was collected with filtration and dried in vacuum, then it was dissolved in N-methylpyrrolidone (NMP) and reprecipitated in water. Yield 1.0 g, T_g 84°C.

Elemental analysis: C 66.54%; H 4.87%; N 3.90%

FT-IR (KBr, cm^{-1}): 884(m), 1103(m), 1205(w), 1339(s), 1448(s), 1588(s), 1685(s), 1700(s), 2980(b), 3300—3600 (b).

2. Thin film preparation

0.1 g synthesized copolymer was dissolved in N, N-dimethylacetamide (DMA, Aldrich) and stirred for one hour. The solution was then filtered through a 0.45 μm Teflon membrane filter and spun-cast onto an indium-tin oxide (ITO) coated

conducting glass producing transparent yellow films. The films were dried in vacuum (10^{-2} torr, 1.33 Pa) at 60°C for 24 hours. The thickness of the copolymer films was determined by using a Tencor Alpha Step 200 profiler after poling and photo-crosslinking. The thickness of the films ranged between 0.5 and $5\text{ }\mu\text{m}$ depending upon the solution viscosity and spinning rate.

3. *In-situ simultaneous photo-crosslinking poling and SHG measurements*

The dried films were poled at elevated temperature using a corona-discharge setup under in-situ conditions described in Ref. [6]. In order to photo-crosslink the films simultaneously, a pen-style UV lamp (power 6 W) was placed perpendicular to film surface with a distance of about 5 cm (Fig. 2). Second harmonic generation (SHG) was measured using the $1.06\text{ }\mu\text{m}$ laser beam from a Q-switched Nd:YAG laser with pulse width of 3 ns and repetition rate of 10 Hz. The incident beam was at 45° to the film normal. The second harmonic coefficients of the films were determined using the calibration techniques reported in Ref. [7].

RESULTS AND DISCUSSION

As well known, cinnamyl group is a photosensitive chromophore and can undergo intermolecular crosslinking with UV irradiation easily, the photo-dimerization between two $\text{C}=\text{C}$ double bonds of cinnamyl group is very effective because of the adjacent carbonyl group which provides desirable polarization towards the reactivity of the double bond. And, the NLO chromophore, 4-nitro-4'-alkoxystilbene which possess higher β value (18×10^{-30} esu in CHCl_3 at $1.908\text{ }\mu\text{m}$ ^[8]; 26×10^{-30} esu in CHCl_3 at $1.91\text{ }\mu\text{m}$ ^[9]) can be introduced into polymer as side chain according to the reactive route of Fig. 1. It can be expected that the photo-crosslinkable NLO active copolymer will be obtained when these two functional chromophores were introduced into the same polymeric backbone. The experiments have confirmed this assumption. The loading levels of chromophore $z (= 1 - x - y$ in Fig. 1) and photo-crosslinkable side group x , which are around 50% and 20% respectively, can be calculated approximately from the ^1H NMR spectrum of (i) the ratio of the integral intensity of broad peak of $\text{CO}-\text{CH}_2-\text{O}-$ at 4.6–5.4 ppm (9 for $2z$ hydrogen) with that of the broad peaks of phenyl ring and ethylene double bond at 6.3–8.4 ppm (57 for $(7x + 10z)$ hydrogen) and (ii) the integral intensity (16) of broad peak at 1.2–2.2 ppm which belongs to CH_2 of backbone. Based on these results the calculated elemental content will be: C 67.27%; H 5.08%; N 3.33%, which coincide with the experimental results well. The copolymer is soluble in strong polar solvents such as NMP, DMA, DMF and DMSO, etc. However, the solubility of films in these solvents are decreased obviously by extending irradiation time. In

general, the poling temperature is selected near films' T_g to achieve higher poling efficiency. In our experiments, the poling temperature must be raised from 90°C to 120°C as extending irradiation, otherwise, the SHG intensity can not be maintained continually. These facts indicate the photo-crosslinking has occurred.

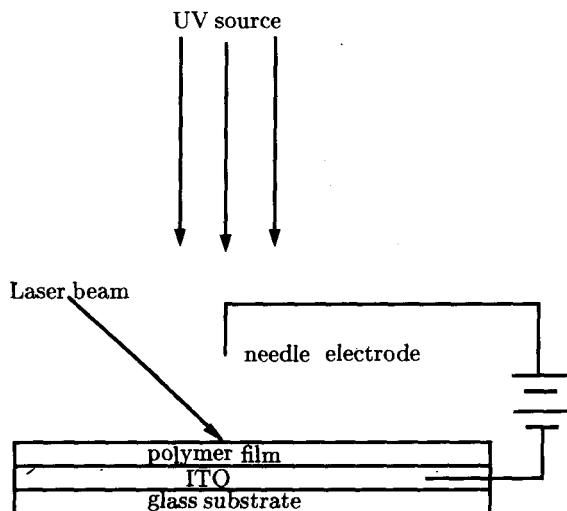


Fig. 2 Scheme of the configuration of in-situ simultaneous photo-crosslinking poling

In situ SHG measurements show that the poled and crosslinked polymer films possess a higher second order nonlinear optical coefficient $d_{33} = 11 \text{ pm/V}$ (i.e. $26.3 \times 10^{-9} \text{ esu}$) which has exceeded the d_{31} of LiNbO_3 ($14.2 \times 10^{-9} \text{ esu}$). As known, the one-dimensional rigid orientation gas model (1D ROGM) has been used to calculate the d_{33} of poled polymer films. For our 50% functionalized film d_{33} will be ranged from 12.3 to 14 pm/V if the order parameter Φ of poled film is 0.3–0.4 which can be easily reached in the case of corona poling. The coincidence of the results of experiment and calculation indicates, as expected, the d value is not decreased by in-situ simultaneous poling and photocrosslinking.

The SHG decay behavior of the copolymer films has been investigated. The temporal decay of SHG intensity for UV-irradiated and non-irradiated films are shown in Fig. 3. In general, the SHG decay can be described with bi-exponential expression of the following equation (1) approximately^[10]:

$$d_{33} \approx Ae^{-t/\tau_1} + Be^{-t/\tau_2} \quad (1)$$

where τ_1 and τ_2 are short- and long-term SHG decay constant, respectively. The latter is the temporal characteristics of d_{33} . Data were fit by least-squares techniques

to obtain the Eq. (2) (irradiated) and Eq. (3) (non-irradiated):

$$Y = 1.00 \times \exp(-0.000205x) \quad (2)$$

$$Y = 0.90 \times \exp(-0.000402x) \quad (3)$$

The τ_2 values are around 5000 and 2500 hours, respectively. It is clear that the temporal decay of irradiated films is quite slower than that of non-irradiated samples. This fact demonstrated that crosslinking is an effective mean to improve the orientation stability of chromophore. Of course, the present τ_2 value of irradiated films are still shorter, it may be caused by limiting crosslink density due to lower power UV lamp used.

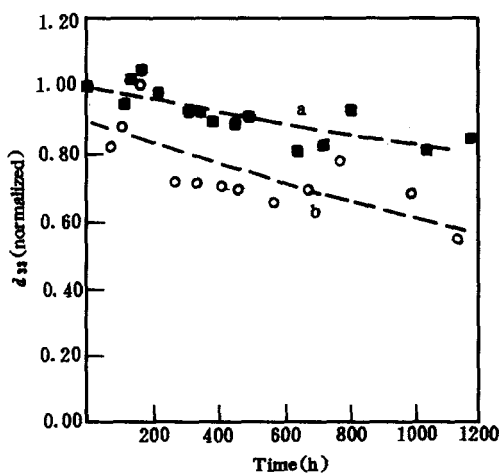


Fig. 3 The SHG decay of irradiated poled (a) and non-irradiated poled (b) films

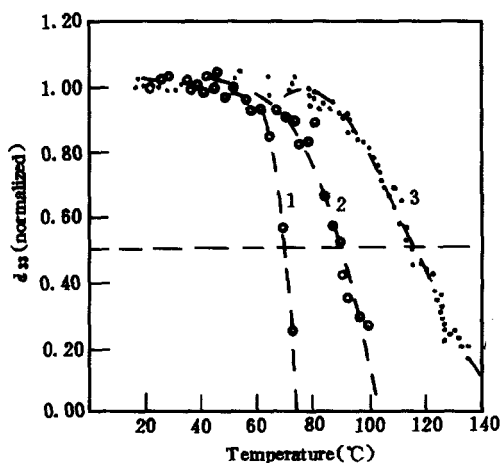


Fig. 4 Temperature dependence of SHG of poled films

1 non-irradiated; 2 irradiated at 104°C for 16 hours; 3 irradiated at 115°C for 17 hours

To investigate the effect of photo-crosslinking on the SHG temporal stability the temperature dependence of SHG for the poled films were studied. After poling and cooling down to room temperature, the applied field was removed. Then the poled films were re-heated at a rate of 4–5°/min, the SHG signal was in-situ monitored. As the temperature rises the signal is decreased, the temperature at which d_{33} is decreased to one half of its value at room temperature is defined as break-over temperature, T_b . In Fig. 4 curve 1 is the result of non-irradiated film poled at 104°C and curve 2, 3 are the results of irradiated poled films which are irradiated for 16 hours at 104°C and 17 hours at 115°C, respectively. It is clear that T_b , which are around 70, 91 and 118°C, has been raised obviously. As well known, the higher is the

T_b of poled films the better is the orientation stability. So, the above results indicate again that temporal stability of poled films has been improved by irradiation. As mentioned above the photo-crosslinking in our experiments was not enough because of the power output of pen-style UV-lamp was low. It can be expected the break-over temperature may be raised further when more effective photo-crosslinking occurs. Except that using higher power UV source and better configuration of experimental setup to introduce more photosensitive chromophore, such as cinnamylidene chloride, as pendant group may be another adaptable route. The work is in progress.

In summary, a photo-crosslinkable side chain type chromophore-functionalized NLO copolymer has been synthesized, the in-situ simultaneous photo-crosslinking poling and SHG measurements demonstrate that the temporal stability of poling-induced chromophore alignment in this copolymer can be significantly enhanced.

Acknowledgment The authors are grateful to Prof. G.K.L. Wong (Department of Physics, Northwestern University, USA) for his helpful discussions and support for the poling and SHG measurements.

Keywords:

Photo-crosslinking; In-situ simultaneous photo-crosslinking poling; Nonlinear optical polymer; SHG; Orientation stability

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