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Simple Preparation of Copolymer of Styrene and 4-Chloromethyl Styrene and Its Application in NLO Materials

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This article reports a synthesis a new class of nonlinear optical (NLO) polymer, containing 3-methyl-4-cyano-5-dicyanomethylidene-2-oxo-3-pyrroline (TCP) acceptor. TCP chromophore was synthesized and characterized by Uv-Vis absorption, ^{1}H NMR, and mass-spectrometry. The titled polymer shows high thermal stability and large optical nonlinearity. A high glass transition temperature of 125°C was determined by DSC measurement, and measured electrooptical (EO) at wavelength 1.31 mm was equal to 37.4 pm/V. The order parameter of these films evaluated by absorption was equal to about 24%.

Keywords: NLO polymer, TCP, chromophore, 4-chloromethyl styrene, electro-optical materials

1. INTRODUCTION

Recently one can observe an enhanced interest to study of organic electrooptical materials, due to their high linear electrooptical (EO) coefficients, ultra fast response times and promising technological abilities, which allows to use them as EO modulators, deflectors, optical switchers.[1-6] Among most of new NLO chromophores prepared recently,[7-10] TCP chromophores show that they possess the larger first order hyperpolarizability caused by a strong electron withdrawing ability of the tricyano-pyrroline acceptor. But this kind of chromophores still have some weak points. The most serious one is that the amide group in their five-section ring made them unstable in most chemical environmenta reaction l.[11,12] Though several researches concerning this kind of chromophores have been reported. Most of the studies were devoted to host-guest system. Such systems give non-sufficient macroscopic electro-optic coefficients. Together with the high degree of chromophore re-orientation.[13-15] To solve these problems, large amounts of side chain polymers have been suggested. The instability of amide in TCP acceptor limited the formation of side chain NLO polymers. As a consequence preparation of a polymer having reactive groups with TCP chromophore was a crucial problem to solve.

Reactivity of the amide group in TCP acceptor has been studied also[16,17] and the reaction between the amide group and benzyl group play here a decisive role. Following this reason, a polymer with chloride benzyl (as a side group) was synthesized in this paper, and the TCP chromophore could be easily attached to this polymer. The polarization efficiency and EO activity were also studied here. Moreover, this polymer also had high glass transition temperature and good film-forming ability, which showed us a good prospect on the optoelectronic devices.

2. EXPERIMENTAL

2.1 Materials and instrumentation

^{1}H NMR spectra were measured on an AVANCE 400 (Bruker) spectrometer using tetramethylsilane (TMS; δ = 0 ppm) as the internal standard. UV-Visible spectra were obtained using a HITACHI U-2001 spectrometer with spectral resolution 1 nm. MS spectra were obtained on MALDI-TOF (Matrix Assisted Laser Desorption/Ionization of Flight) on BIFLEX III (Bruker Inc.). The DSC curves were recorded with a TA-instrument Q10 analyzers with a heat rate of 10 K/min under nitrogen atmosphere.

2.2 Synthesis of chromophore

2.2.1 Malononitrile dimer

Malononitrile (33 g, 0.5 mol) was dissolved in the mixture of 200 mL THF and 100 mL ether. Then Sodium sand (6 g, 0.25 mol) was added successively to the solution. The mixture was stirred at room temperature for 1 hour, and then was refluxed for 24 hours. After filtering, the solid was collected and added to ice water (300 mL), and then concentrated hydrochloric acid (15 - 20 mL) was added to the water solu-

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*Corresponding author: liujialei@mail.ipc.ac.cn tion. The malononitrils dimmer would precipitate slowly as crystal. Melting point was 169°C - 172°C. The yield was 20 g (61%).

2.2.2 TCP acceptor

Malononitrile dimer (2.64 g, 10 mmol) was dissolved in ethanol (50 mL), and then ethyl pyruvate (2.55 g, 11 mmol) was added to the solution. The mixture was refluxed under N_2 for 1 h. Afterwards the ethanol was evaporated, the solid was dissolved in dichloromethane (50 mL); and most of the remaining malononitrile dimer was removed. The TCP acceptor was purified with column chromatography using the dichloromethane as solvent. The yield was about 0.85 g (23%). 1H NMR ($CDCl_3$): δ2.39 (3H, s), 8.75 (1H, s).

2.2.3 TCP chromophore

To a solution of TCP acceptor (of 0.37 g, 2.0 mmol) solvated in 10 mL of ethanol 4-(N,N-diethylamine)benzaldehyde (0.71 g, 4.0 mmol) was added, and the mixture was heated at 60°C under argon for 45 min to complete the reaction. The resulting reaction mixture is cooled, filtered, washed with cool ethanol and dried to give 0.45 g (65%) of pure TCP chromophore. 1H NMR (CD_3COCD_3): δ: 7.82 (1H, d), 7.79 (2H, d), 6.85(2H, d), 6.70 (1H, d), 5.2 (1H, s), 3.79 (4H, m), 1.29 (6H, t). UV-Vis (CH_3COCH_3): λ_{max} = 702 nm, ν_{max}, chloroform). (MALDI-TOF), m/z: 343.2 (M^+).

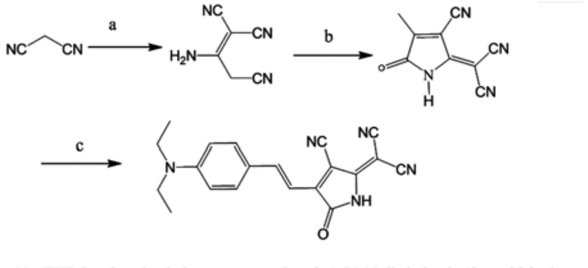
2.2.4 Synthesis of the polymer

2.2.4.1 Polymer 1

Vinyl benzene (2.08 g, 20.0 mmol), 4-chloromethyl styrene (1.52 g, 10 mmol), and azobisisobutyronitrile (AIBN, 0.08 g, 0.5 mmol) were dissolved in THF (30 mL) under nitrogen. The mixture was stirred at 65°C for 24 hour to yield a viscous solution. The resulting product was poured into hexane to induce precipitation. The polymer was collected by filtration, washed with hexane several times, and dried at 40°C in vacuo. The yield was 2.91 g (81%).

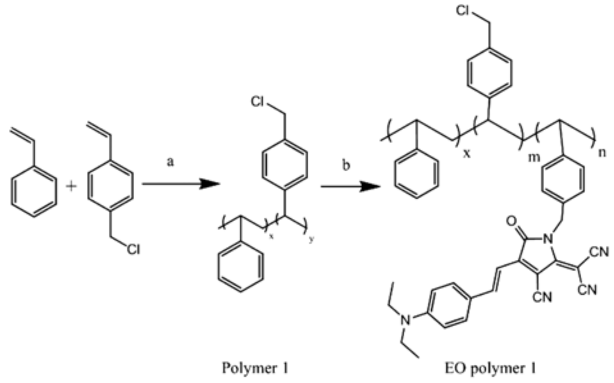
2.2.4.2 EO polymer 1

Polymer 1 (1 g), TCP chromophore (0.3 g) and anhydrous potassium carbonate (0.2 g) was added to DMF (20 mL). The mixture was stirred at 70°C for 1 hour, and then was poured into 100 mL water. After filtering, the green solid was collected. The green solid was dissolved in DMF and washed with ether for 3 times. Pure EO polymer was prepared; the yield was 0.65 g (54%).



a. Na, THF; b. ethanol, ethyl pyruvate; c. ethanol, 4-(N, N-diethylamine)benzaldehyde

Sheme 1. The synthesis of TCP chromophore.



a. AIBN, toluene; b. K2CO3, DMF

Sheme 2. The synthesis of polymer 1 and EO polymer 1.

2.3 Preparation of poled polymer films and EO coefficient

Films were prepared on glass substrate from cyclopentanone solution. Firstly, the polymers and chromophores were dissolved in cyclopentanone completely, and then the solution was filtered to remove particle impurities, spun at 800 rpm and dried under vacuum to ensure removal of any residual solvent. After that, smooth and neat films of 2 - 3 μm were obtained. The poling processes for the second-order NLO polymer films were carried out using a corona poling technique. The temperature was raised slowly from ambient temperature to the poling temperature (T_p), which is approximately 5 K higher than the T_g of the sample. When the temperature reached T_p, the poling voltage was applied and followed to maintain the poling voltage at T_p for 30 - 50 min. The poling voltage 8 - 9 KV were used to explore the best poling voltage for the films. After cooling to ambient temperature and switching off of the poling field, the EO coefficients of the poled films were monitored at wavelength 1310 nm using simple reflection technique proposed by Teng and Man.

3. RESULTS AND DISCUSSION

The performed studies have shown that side chain NLO polymers have good orientationally alignment stability, polarization efficiency and solubility.[18,19] TCP chromophore as a group of new NLO chromophore has a large first-order hyperpolarizability which is the the crucial for the EO materials' EO coefficient. However, due to instability of the amide group in the pyrroline cycle, it is difficuly to attach the chromophore to a suitable polymer as a side chain. The yield of the reaction between TCP chromophore and benzyl chloride is very high. Thus, we designed and synthesized a polymer with benzyl chloride group as a side chain for connecting TCP chromophore.

The synthesis of TCP chromophore was shown in Scheme 1. It was started by malononitrile; the malononitrile dimmer was prepared from malononitrile in the strong alkaline environment, then the malononitrile dimmer reacted with ethyl pyruvate to obtain TCP acceptor; and at last, the TCP chromphore was synthesized by the Knoevengel condensation reaction of TCP acceptor and 4-(N,N-diethylamine)benzaldehyde.

The synthesis of polymer is shown in Scheme 2. Styrene, 4-chloromethyl styrene was received from TCI Company. Polymerization was occurred in the solution of toluene, under the nitrogen atmosphere, at the temperature of 70°C. Being washed for several times, the polymer was dissolved in DMF, then, anhydrous potassium carbonate and TCP chromophore was added to the solution, the mixture was stirred at 65°C for 2 hours, and poured to water. Then dilute hydrochloric acid was added by drop wise until the solution became neutral. After filtering, the EO polymer was collected as a green solid power. The chemical structure of polymer and EO polymer was monitored by NMR spectra, ^{1}H NMR spectrum of the polymers was given in Fig. 1 and 2. Due to the solubility of the polymers, NMR of the polymer 1 was characterized in $CDCl_3$; EO polymer 1 and was characterized in DMF.

The composition of the polymer was controlled by ^{1}H NMR. Figure 1 shows the ^{1}H NMR spectrum of Polymer **1** and the assignment of peaks in the downfield. The composition was evaluated from the integration area of two phenyl protons in the range of 6.00 - 7.50 ppm and the protons of $-CCH_2Cl$ groups at 4.5 ppm. It can be easily known that the ratio of Styrene and 4-chloromethyl styrene is about 6 : 1.

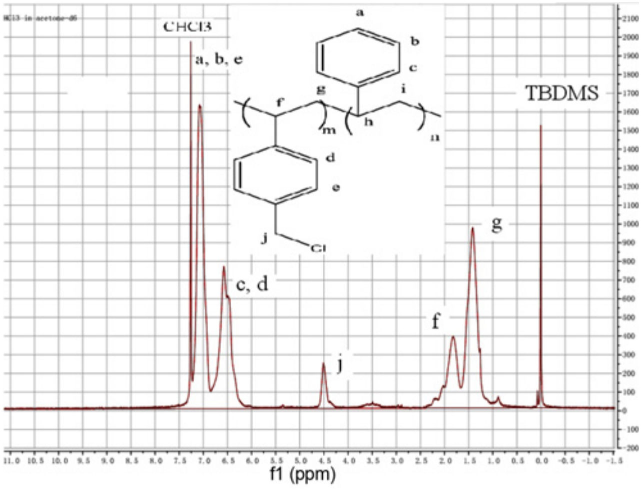


Fig. 1. ^{1}HNMR of polymer 1.

After the post coupling reaction, it can be known that the chromophore loading density is about 17.5% by weight from Fig. 2.

Glass transition temperature is an important characterization of EO polymers, which determines the quality of the film forming and alignment stability of the orientation of the NLO chromophores.[20] The T_g for this EO polymer is 125°C (as shown in Fig. 3), which was studied by DSC under nitrogen with a heating rate of 10 ^{K}/min. During the preparation of the EO devices, high temperature was needed, and 125°C was sufficient for these processes. So this kind of polymer can be used for EO devices fabrication, which would be reported else where.

Figure 4 shows us the Uv-vis spectrum before and after corona poling of the EO films, which is related with the order parameter of EO film. It could intuitively reflect the poling efficiency of the EO films. From the absorption change, order parameter (ϕ) for EO films was evaluted fol-

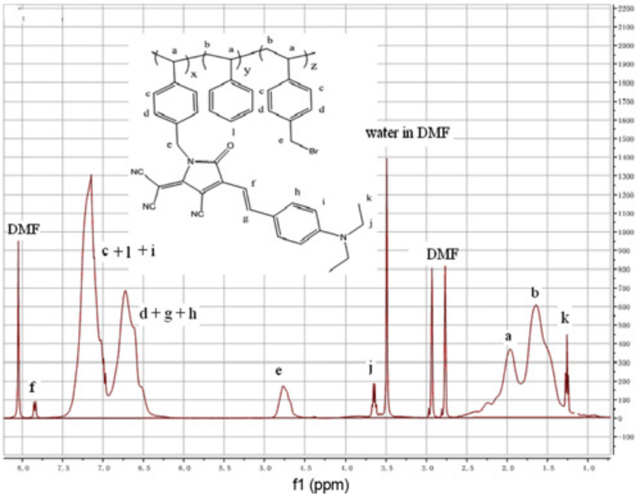


Fig. 2. ^{1}HNMR of EO polymer 1.

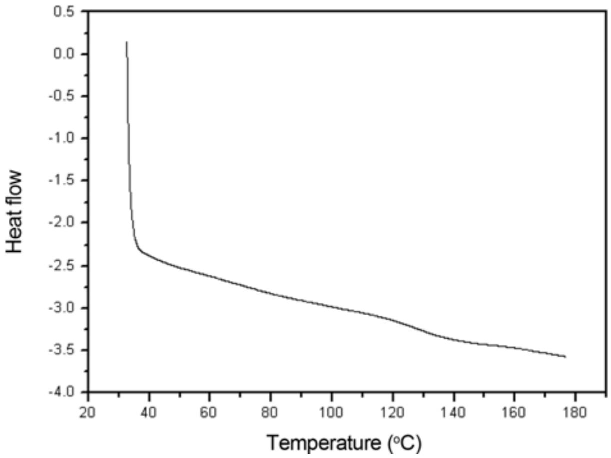


Fig. 3. Differential scanning calorimetry (DSC) trace of EO polymer recorded under nitrogen flow with a scanning rate of 10°C min^{-1}.

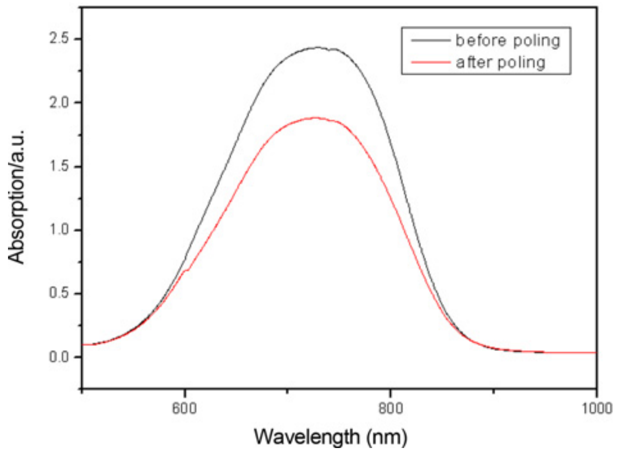


Fig. 4. Uv-vis spectrum before and after corona poling of the EO film.

lowing the equation:

$$\phi = 1 - A_1/A_0$$

where A_1 and A_0 are the absorbance of the EO film after and before corona poling, respectively. Order parameter of this EO film is about 24% and it is relatively large with respect to the TCP chromophore in the doping system.

The r_{33} measurement at the laser wavelength of 1.31 nm was performed by a Teng-Mann reflection method.[21,22] It was calculated according formula (1) :

$$r_{33} = \frac{3\lambda I_m}{4\Pi V_m I_c n^2} \cdot \frac{(n^2 - \sin^2\theta)^{1/2}}{\sin^2\theta} \qquad (1)$$

where I_m is the amplitude of the modulation, λ is the wavelength of the light, V_m is the modulating voltage, I_c is half the maximum laser intensity, n is the index of refraction, θ is the incident angle. The r_{33} for this EO film is equal to about 37.4 pm/V and compared with the doped system (26 pm/V), it is improved up to 40%. Else, the orientation stability was also improved; there was no clearly drop down of the EO coefficient 100 days after the EO film was poled.

In a NLO material, the EO coefficients (r_{33}) value depends on many factors, such as first hyperpolarizability of chromophore molecular, chromophore number density, poling efficience. An operational equation for the principal element of the electro-optic tensor (r_{33}) for an organic material consisting of dipolar chromophores, is[23]

$$r_{33} = \beta(\varepsilon, \omega) N < \cos 3\theta > F(\varepsilon, n) \qquad (2)$$

Where β (ε, ω) is the molecular first hyperpolarizability (which depends on dielectric permittivity (ε) and upon optical frequency (ω)), N is chromophore concenrtation (molecules/cc). <cos3θ> is the acentric order parameter which depends on poling conditions and inter-molecular electrostatic interactions, and $F(\varepsilon, n)$ is a constant that depends upon dielectric permittivity and index of refraction. Compared with doping system, the side chain EO polymer can separate and fix the chromophore molecules, <cos3θ> in formula (2) could be increased greatly; else, the effective chromophore number density (N) could also be improved. So the enhancement of the r_{33} for this EO polymer is reasonable, compared with the doping system. Addiitonally some role play vibration subsyem.[24]

4. CONCLUSIONS

A novel polymer containing active side group (benzyl chloride) was designed and synthesized for the application of TCP chromophore. TCP chromophore can be easily added to the polymer as a larger side chain to form an EO polymer. TCP chromophore was synthesized and characterized by Uv-Vis spectra, ^{1}H NMR, and Mass spectrometry. Polymer **1** and EO polymer **1** were verified by NMR spectra. EO films made from this EO polymer show us good thermal performance and the EO coefficient (37.4 pm/V) was improved greatly, according to the doping system, and therefore it can be considered as a potential candidate for optoelectronics applications.

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