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Novel, side-on, PVK-based nonlinear optical polymers: Synthesis and NLO properties

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ABSTRACT

A novel, poly(vinylcarbazole)-based nonlinear optical polymer (side-on type), in which the chromophore was attached to the polymer backbone at the centre of the D-π-A bridge, was synthesized conveniently via the post-Knoevenagel condensation reaction. The structure of chromophore was further modified by the introduction of an isolation spacer (carbazole group) to improve poling efficiency. The ensuing polymer displayed good solubility and high thermal stability and its poled film exhibited a relatively large d_{33} value of $\leq$56.0 pm/V.

1. Introduction

Considerable efforts have focused on organic nonlinear optical (NLO) polymers over the past few decades, owing to such compounds displaying advantages over inorganic materials, including large NLO effects, mechanical endurance, low driving voltage and ease of processing [1–5]. In order to realize their huge potential for use in photonic devices, such as telecommunications, optical data storage and THz generation, NLO materials should demonstrate large macroscopic optical nonlinearity, high physical and chemical stabilities as well as good optical transparency [1–11]. However, the achievement of all of these requirements simultaneously presents a major obstacle, one of note being that high molecular nonlinearity (β) of a chromophore cannot be efficiently translated into high macroscopic NLO activity of a polymer. Generally, during the poling-induced noncentrosymmetric alignment of chromophores, which is required to secure macroscopic NLO effects, the poling efficiency of the materials is significantly reduced owing to the strong intermolecular, dipole–dipole interactions of the highly polar chromophore [12–15]. By controlling the shape of the chromophore moieties according to the site isolation principle, such interactions can be minimized and poling efficiency enhanced dramatically [16,17]. Dalton and Jen et al. prepared a series of dendrimers and polymers containing dendronized chromophores, which displayed very large macroscopic optical nonlinearity [18–22]. The author's research group is interested in the design and synthesis of novel NLO materials and the relationship between structure and properties [23–32]; recent papers [26–32] have revealed that the macroscopic nonlinearity of NLO polymers could be boosted several times by binding suitable 'isolation groups' to NLO chromophore moieties [26–32].

A novel, postfunctionalization method was used to prepare a PVK-based NLO polymer, which exhibited good long term stability of the NLO effect (the NLO activity remains unchanged at 120 °C for over 1000 h after a minor initial drop), but it possessed relatively low d_{33} value (20 pm/V) [33]. A series of PVK-based NLO polymers with sulfonyl-groups as acceptor in the chromophore moieties were prepared, in which different isolation spacers were introduced, and the polymers exhibited good comprehensive properties [34], confirming that PVK was a good parent polymer to be further functionalized for the preparation of promising PVK-based NLO materials.

In contrast, in the majority of side-chain NLO polymers reported, the typical linkage position on the D-π-A system was at the end of the donor or acceptor side in the chromophore groups, which could be termed as end-on side-chain polymers [23,24,33,34]. Although very scarce, there is another type of NLO polymers (side-on type), namely, one in which the site for the introduction of the

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chromophore within the polymer backbone is at the centre of the π bridge [35–38]. Jen et al. prepared a series of this type of side-chain dendronized NLO polymers by covalently attaching the chromophore moieties to the centre of the π-bridge in the polymeric backbone; the ensuing compounds displayed high dielectric strength, excellent optical quality, good processability, and reliable poling behaviors [39]. The current research group also has carried out similar work, and obtained several NLO polymers with good performance [28,29]. Thus, considering the low poling efficiency of our previous PVK-based polymers, we sought to apply this side-on mode to PVK-based NLO polymers. This paper concerns the synthesis of a novel, side-on PVK-based NLO polymer, in which the linkage position on the chromophore group was in the middle of its D-π-A bridge, and, as such, differs from previously reported PVK-based polymers [33,34]. Carbazole moieties were used as isolation groups, which have been confirmed as the suitable isolation groups for the nitro-based chromophores in our previous work [26], according to the concept of “suitable isolation groups”. The resultant polymer demonstrated excellent solubility, good thermal ability, and relatively high d_{33} value (56.0 pm/V). Herein, we would like to report the synthesis, characterization and NLO properties of this PVK polymer Schemes 1 and 2.

2. Experimental section

2.1. Materials

Tetrahydrofuran (THF) was dried over and distilled from K–Na alloy under an atmosphere of dry nitrogen. *N*,*N*-Dimethylformamide (DMF) was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen. Dichloromethane (CH_2Cl_2) was dried over anhydrous $CaCl_2$ and fresh distilled before use. Poly(*N*-vinylcarbazole) (PVK) was purchased from Aldrich, and its weight-averaged molecular weight was estimated to be 1.10×10^6. **PVK-CHO** (**P0**) was synthesized according to our previous work [33]. Compounds **3** and **5** were synthesized according to our previous work [26,40]. All other reagents were used as-received.

2.2. Instrumentation

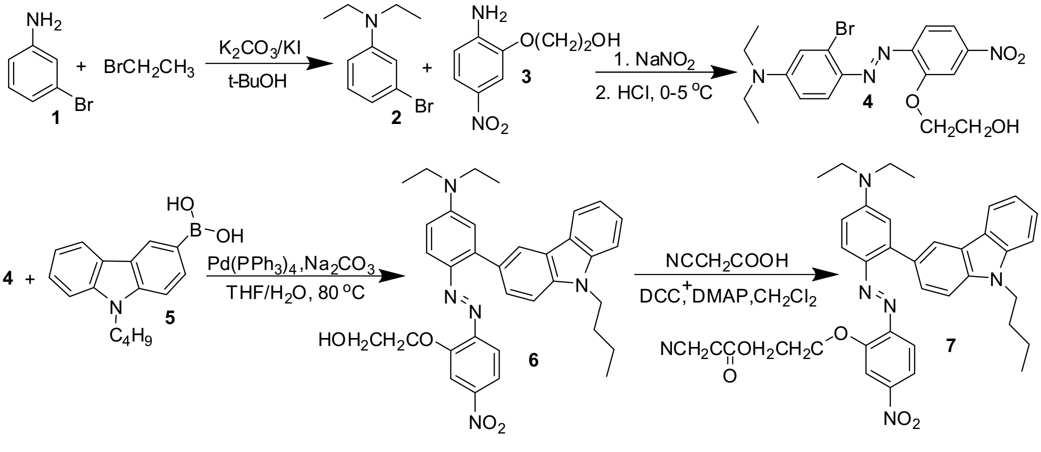
^{1}H and ^{13}C NMR spectra were measured on a Varian Mercury300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer-2 spectrometer in the region of 3000–400 cm^{-1} on NaCl pellets. UV–vis spectra were obtained using a Shimadzu UV-2550 spectrometer. Gel permeation chromatography (GPC) was used to determine the molecular weights of polymers. GPC analysis was performed on a Waters HPLC system equipped with a 2690D separation module and a 2410 refractive index detector. Polystyrene standards were used as calibration standards for GPC. DMF was used as eluent, and the flow rate was 1.0 mL/min. EI-MS spectra were recorded with a Finnigan PRACE mass spectrometer. Elemental analyses were performed by a CARLOERBA-1106 micro-elemental analyzer. Thermal analysis was performed on NETZSCH STA449C thermal analyzer at a heating rate of 10 °C/min in nitrogen at a flow rate of 50 cm^3/min for thermogravimetric analysis (TGA). The thermal transitions of the polymers were investigated using a METTLER differential scanning calorimeter DSC822e under nitrogen at a scanning rate of 10 °C/min. The thermometer for measurement of the melting point was uncorrected. The thickness of the films was measured with an Ambios Technology XP-2 profilometer.

2.3. Synthesis of compound **2**

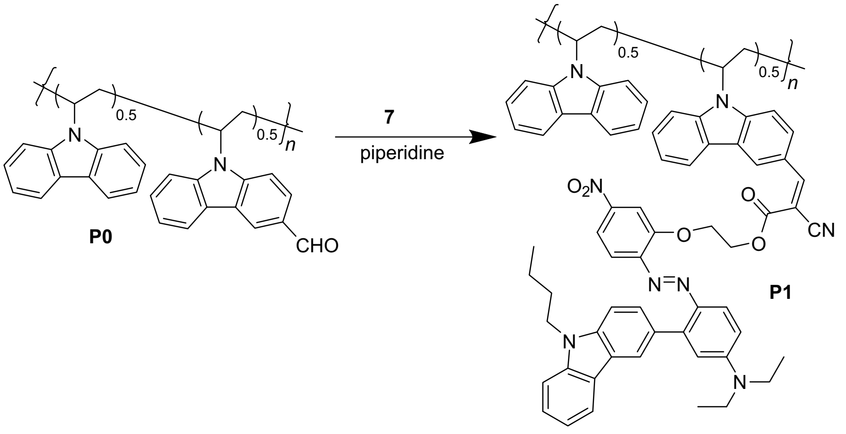
3-Bromoaniline (**1**) (5.16 g, 0.03 mol) and bromoethane (9.81 g, 0.09 mol) were dissolved in *t*-BuOH (50 mL) in the presence of potassium carbonate (13.80 g, 0.10 mol) as an acid acceptor with potassium iodide (0.60 g, 3.60 mmol) as catalyst. The resultant mixture was stirred at 100 °C for 2 days. Then the residue was filtered, and most of the solvent in the filtrate was removed under reduced pressure. The crude product was purified with column chromatography on silica gel using ethyl acetate/petroleum ether (1/5) as eluent to afford brown oil **2** (3.00 g, 43.9%). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.15 (t, $J = 7.5$ Hz, 6H, $-CH_3$), 3.33 (q, $J = 6.6$ Hz, 4H, $-N-CH_2-$), 6.55 (d, $J = 8.7$ Hz, 1H, ArH), 6.77 (m, 2H, ArH), 7.04 (t, $J = 8.1$ Hz, 1H, ArH).

2.4. Synthesis of chromophore **4**

4-Nitroaniline (**3**) (105 mg, 0.53 mmol) was dissolved in a water solution of 35% hydrochloric acid. The mixture was cooled to 0–5 °C in an ice bath, and then a solution of sodium nitrite (41 mg, 0.59 mmol) in water was added to the above solution dropwise. After stirred below 5 °C for 15 min, a solution of **1** (114 mg, 0.50 mmol) in ethanol was added slowly. The mixture was left in the ice bath for another 1 h, some sodium bicarbonate was added to adjust the pH value to about 7.0. The reaction mixture was stirred for another 0.5 h, the red precipitate was filtered, washed with water. The crude product was purified by recrystallization from



Scheme 1.



Scheme 2.

ethanol/water to afford deeply red powder (120 mg, 55.0%). Mp = 138–140 °C. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.23 (t, $J = 7.5$ Hz, 6H, –CH_3), 3.44 (q, $J = 7.2$ Hz, 4H, –N–CH_2–), 4.01 (br, s, 2H, –O–CH_2–), 4.36 (t, $J = 6.9$ Hz, 2H, –O–CH_2–), 6.62 (dd, $J = 1.5$, 8.7 Hz, 1H, ArH), 6.97 (s, 1H, ArH), 7.77 (m, 2H, ArH), 7.94 (m, 2H, ArH).

2.5. Synthesis of compound 6

A mixture of compound **4** (110 mg, 0.26 mmol), 3-*N*-(*n*-butane) carbazole boronic acid (**5**) (88 mg, 0.30 mmol), sodium carbonate (276 mg, 2.60 mmol), THF (9 mL)/water (3 mL), and $Pd(PPh_3)_4$ (10 mg) was carefully degassed and charged with nitrogen. Then the reaction mixture was stirred at 80 °C for 30 h. After cooled to room temperature, the mixture was extracted by $CHCl_3$. The crude product was purified by chromatography on silica gel using ethyl acetate/petroleum ether (1/1) as eluent to afford deeply red solid (138 mg, 93.9%). Mp = 167–168 °C. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.98 (t, $J = 7.2$ Hz, 3H, –CH_3) 1.29 (t, $J = 6.6$ Hz, 6H, –CH_3), 1.45 (m, 2H, –CH_2–), 1.92 (m, 2H, –CH_2–), 3.53 (q, $J = 6.6$ Hz, 4H, –N–CH_2–), 4.00 (br, s, 2H, –O–CH_2–), 4.37 (m, 4H, –N–CH_2– and –O–CH_2–), 6.74 (dd, $J = 2.7$, 9.0 Hz, 1H, ArH), 6.85 (s, 1H, ArH), 7.21 (m, 1H, ArH), 7.47 (m, 4H, ArH), 7.62 (d, $J = 8.7$ Hz, 1H, ArH), 7.69 (dd, $J = 1.5$, 9.0 Hz, 1H, ArH), 7.93 (m, 2H, ArH), 8.06 (d, $J = 7.8$ Hz, 1H, ArH), 8.23 (s, 1H, ArH).

2.6. Synthesis of compound 7

Chromophore **6** (128 mg, 0.22 mmol), cyanoacetic acid (23 mg, 0.28 mmol), dicyclohexylcarbodiimide (DCC) (71 mg, 0.34 mmol), 4-(*N*,*N*-dimethyl)aminopyridine (DMAP) (5 mg, 0.04 mmol) were dissolved in proper dry CH_2Cl_2 and stirred at room temperature for 24 h. The precipitate was filtered and the crude product was purified by column chromatography using ethyl acetate/dichloromethane (1/20) as eluent to afford deeply red solid (120 mg, 84.5%). Mp = 126–128 °C. IR (thin film), υ (cm^{-1}): 1754 (C=O), 1518, 1331 (–NO_2). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.99 (t, $J = 7.2$ Hz, 3H, –CH_3) 1.30 (t, $J = 6.6$ Hz, 6H, –CH_3), 1.45 (m, 2H, –CH_2–), 1.90 (m, 2H, –CH_2–), 3.54 (m, 6H, –CH_2CN and –N–CH_2–), 4.35 (t, $J = 7.2$ Hz, 2H, –N–CH_2–), 4.48 (t, $J = 4.5$ Hz, 2H, –O–CH_2–), 4.72 (t, $J = 4.5$ Hz, 2H, –O–CH_2–), 6.80 (m, 2H, ArH), 7.22 (m, 1H, ArH), 7.47 (m, 4H, ArH), 7.64 (dd, $J = 1.8$, 9.0 Hz, 1H, ArH), 7.69 (dd, $J = 2.4$, 9.0 Hz, 1H, ArH), 7.85 (d, $J = 2.4$ Hz, 1H, ArH), 7.86 (d, $J = 9.6$ Hz, 1H, ArH), 8.06 (d, $J = 7.8$ Hz, 1H, ArH), 8.24 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$) δ (ppm): 13.08, 14.18, 20.86, 24.96, 31.45, 43.25, 45.16, 64.90, 68.30, 107.89, 109.13, 110.85, 111.37, 112.41, 113.03, 118.01, 118.10, 118.42, 119.25, 120.42, 122.60, 122.98, 123.22, 126.00, 129.08, 130.53, 140.26, 141.11, 141.65, 147.54, 148.01, 151.45, 154.63, 163.30. MS (EI), m/z [M$^+$]: 646.5, calcd: 646.3. $C_{37}H_{38}N_6O_5$ (EA) (%, found/calcd): C, 68.20/68.71; H, 6.17/5.92; N, 12.62/12.99. UV–vis (DMF, 2.5×10^{-5} mol/L): λ_{max}: 515 nm; ε_{max}: 2.68×10^4 mol^{-1} L cm^{-1}.

2.7. Synthesis of polymer P1

PVK-CHO (**P0**) (27 mg) was dissolved in DMF (2 mL), then a solution of chromophore **7** (105 mg, 0.16 mmol) dissolved in THF (2 mL) and a catalytic amount of piperidine were added under an atmosphere of dry nitrogen. The reaction mixture was stirred at 45 °C for 48 h, then dropped into methanol. The obtained precipitate was filtered and washed with methanol for several times. The resultant product was collected and dried under vaccum at 40 °C (60 mg, 55.1%). $M_w = 7.35 \times 10^5$, $M_w/M_n = 1.31$ (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 2220 (CN), 1719 (C=O), 1671, 746, 722 (carbazole), 1519, 1335 (–NO_2). ^{1}H NMR (DMSO-d_6) δ (ppm): 0.7–1.0 (–CH_3), 1.0–1.3 (–CH_3), 1.4–1.9 (–CH_2–), 3.6–3.8 (–NCH_2–), 4.1–4.4 (–NCH_2– and –OCH_2–), 4.7–4.9 (–CH_2–), 6.7–6.9 (ArH), 7.0–7.2 (ArH), 7.3–7.6 (ArH), 7.7–7.9 (ArH), 8.0–8.3 (ArH). UV–vis (DMF, 0.01 mg/mL): λ_{max} (nm): 516 nm.

3. Results and discussion

3.1. Synthesis and characterizations

The detailed synthetic procedure of chromophore **7** is presented in Scheme 1, and the overall route was simple and with moderate yield. 3-Bromo-bisethyl-aminobenzene (**2**) was prepared by the reaction between 3-bromoaniline (**1**) and bromoethane, similar to our previous work [26]. Under the normal azo coupling reaction conditions, chromophore **4** with two functional groups (aryl bromine and hydroxyl group) was conveniently yielded, which could react with 3-*N*-(*n*-butane) carbazole boronic acid (**5**) to afford chromophore **6** with high yield, through Suzuki coupling reaction. Then, the cyanoacetylated chromophore **7** was prepared successfully by the reaction of chromophores **6** with cyanoacetic acid under mild conditions. Finally, by Knoevenagel condensation reaction, the PVK-based NLO polymer (**P1**) was conveniently obtained between the partially formylated PVK (**P0**) and the corresponding chromophore (**7**) with the satisfied yield (55.1%).

3.2. Structure characterization

The chromophores and polymer were characterized by spectroscopic methods, and all gave satisfactory spectral data (see

Experimental section for detailed analysis data). As shown in Fig. 1, the strong absorption band of the formyl groups at 1690 cm^{-1} in **P0** disappeared after the reaction between **P0** and chromophore **7**, and the new absorption bands in **P1** at about 1719 and 2220 cm^{-1}, were ascribed to the carbonyl stretching vibration of a conjugated carboxylic ester and the nitrile stretching vibration respectively, while the typical absorption peak of nitro groups appeared at about 1519 and 1330 cm^{-1}. All these changes indicated that the chromophore moieties were successfully bonded to the polymer backbone. In addition, in the ^1H NMR spectra of **P1**, the absorption peak of the aldehyde groups disappeared, proving the almost complete conversion of the formyl groups of **P0** to chromophore-functionalized PVK-based polymer, due to high reactivity of the formyl groups towards the active methylene species in the cyanoacetate *via* the Knoevenagel condensation reaction.

P1 was well soluble in common polar organic solvents, such as DMF, DMSO, and NMP, since the introduced isolation groups suppressed the polymer inter-chain entanglements. The UV–vis absorption spectra of **P0**, **P1** and the corresponding chromophore (**7**) in DMF solutions are shown in Fig. 2. The polymers exhibited weak absorption bands of the carbazole group at about 324 nm, and the maximum absorption wavelength of the azo moieties was at about 515 nm (listed in Experimental section). Moreover, the maximum absorption wavelength at 407 nm should be attributed to the charge transfer of [2-cyano-3-[9-alkyl substituted] carbazolyl]-acrylate chromophore, indicating the success of polymer reaction.

The molecular weights of polymer were determined by gel permeation chromatography (GPC) with DMF as an eluent, with polystyrene standards as calibration standards, and the M_w was 7.35×10^5 and M_w/M_n was 1.31. As shown in Fig. 3, the thermal stability, determined by TGA, displayed that the polymer was thermal stable up to 235 °C, and the glass transition temperature of **P1** was tested to be 116 °C using a Setaram differential scanning calorimeter (DSC). Compared to our other PVK-based polymers, **P1** exhibited relatively low glass transition temperature, the possible reason should be that this shape of chromophores created much more free volume, which decreased the rigidity of PVK backbone in some degree.

3.3. NLO properties

To evaluate the NLO activity of the polymer, its poled thin films were prepared. The convenient technique to study the second-order NLO activity is to investigate the second harmonic generation (SHG) processes characterized by d_{33}, an SHG coefficient. Calculation of the SHG coefficients (d_{33}) for the poled films is based on the equation given below:

$$\frac{d_{33,s}}{d_{11,q}} = \sqrt{\frac{I_s l_{c,q}}{I_q \; l_s}}\,F \tag{1}$$

where $d_{11,q}$ is d_{11} of the quartz crystals, which is equal to 0.45 pm/V. I_s and I_q are the SHG intensities of the sample and the quartz, respectively, $l_{c,q}$ is the coherent length of the quartz, l_s is the thickness of the polymer film, and F is the correction factors of the apparatus and equals to 1.2 when $l_c >> l_s$. From the experimental data, the d_{33} value of **P1** was calculated to be 56.0 pm/V at fundamental wavelength of 1064 nm. And by using the approximation two-level model, the nonresonant d_{33} value was estimated to be 3.0 pm/V. In comparison with our reported PVK-based polymers [33,34], here, **P1** exhibited relatively high NLO effect, related to the isolation effects and its unique approach of the chromophore attaching into polymer-chain. Firstly, carbazole groups were

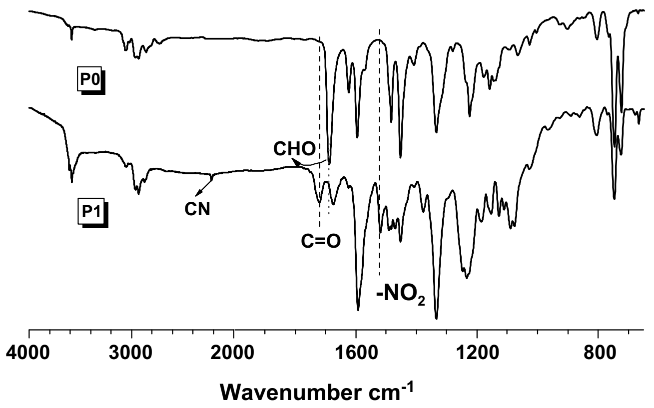


Fig. 1. IR spectra of polymers **P0** and **P1**.

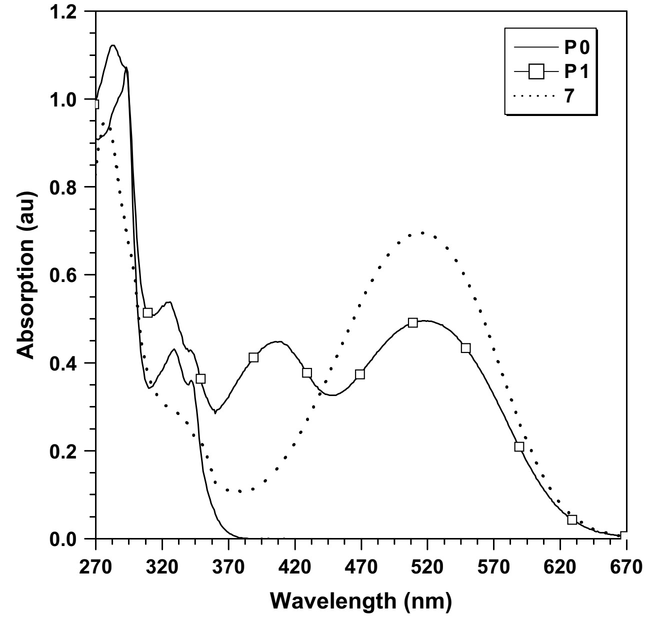


Fig. 2. UV–vis spectra of *N,N*-dimethylformamide (DMF) solutions of polymers **P0–1** (0.02 mg/mL) and chromophores **7** (2.5×10^{-5} mol/L).

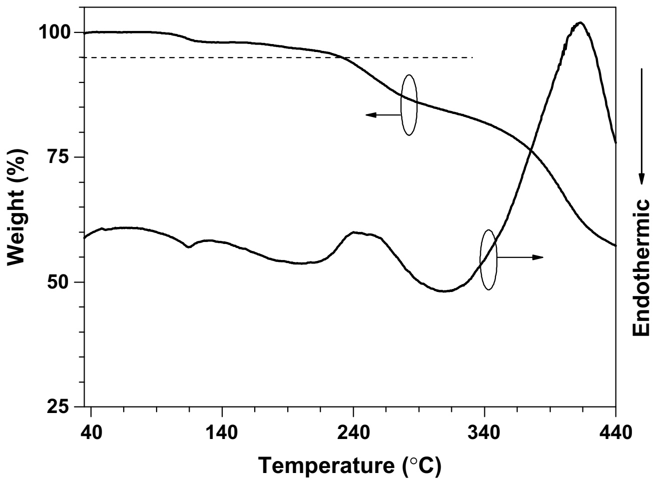


Fig. 3. DSC and TGA curves of **P1** at a heating rate of 10 °C/min under N_2 atmosphere.

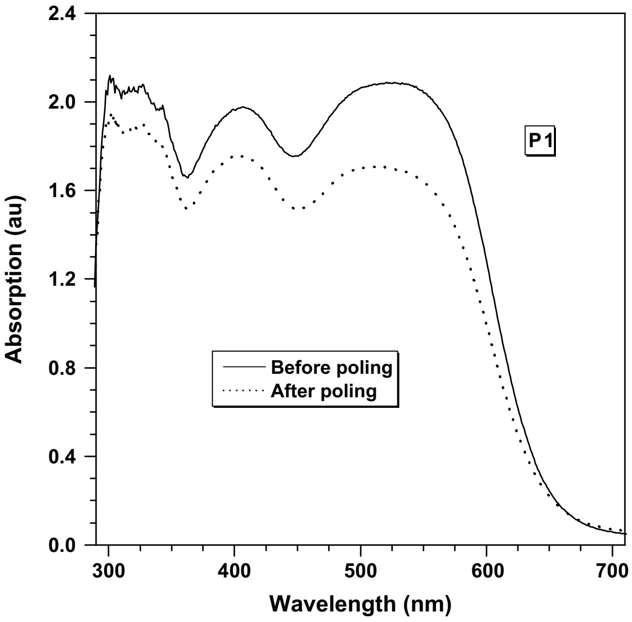


Fig. 4. Absorption spectra of the film of **P1** before and after poling.

introduced into the chromophore in the π-bridge near the donor side, which could efficiently reduce the intermolecular electrostatic dipole–dipole interactions, and lead to the enhanced macroscopic nonlinearity, according to our previous work [26]. Also, it should be ascribed to the new linkage mode of chromophore moieties (in the middle of its π-bridge) in the side-chain of the polymer, which was demonstrated to be superior to that end-on connecting approach, based on the literatures [35,39]. For this side-on type of polymers, the structure would be more 3-D extended and the steric hindrance could be reduced for chromophore reorientation, which could directly improve the poling efficiency efficiently. To further study the chromophore dipole alignment of **P1**, the order parameter (Φ) was measured. Fig. 4 shows the UV–vis spectrum of the film of **P1** before and after corona poling. After the corona poling, the dipole moments of the chromophore moieties in the polymer were aligned, and the absorption curve decreased due to birefringence. From the absorption change, the Φ value for polymer can be calculated according to the following equation:

$$\Phi = 1 - A_1/A_0 \tag{2}$$

where A_1 and A_0 are the absorbances of the polymer film after and before corona poling, respectively. Then, the Φ value of **P1** was calculated to be 0.18, indicating good chromophore alignment during the poling-induced process.

4. Conclusions

For the first time, a new side-on PVK-based NLO polymer, with structure different from our previously reported PVK-based polymers, was prepared successfully, in which carbazole groups were introduced as isolation groups, and the linking position of the chromophore was in the middle of the π-bridge. This might be an alternative approach to design good NLO polymers, by using carbazole-like bulky conjugated moiety as an isolation groups and the linkage of the large conjugated chromophore in the middle of the π-bridge. The resultant polymer demonstrated excellent solubility, good thermal ability, and relatively high d_{33} value (56.0 pm/V), making it promising candidate for practical applications in photonic fields.

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