A Postfunctionalization Strategy To Develop PVK−Based Nonlinear Optical Polymers with a High Density of Chromophores and Improved Processibility

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A new strategy for postfunctionalization performed on poly(*N*-vinylcarbazole) (PVK) has been explored to develop PVK-based nonlinear optical (NLO) polymers with a high density of chromophores and improved comprehensive properties. Thus, under the standard Vilsmeier reaction conditions, PVK is partially formylated to a high degree (up to 52% molar ratio), and these formyl groups of high reactivity are condensed with cyanoacetylated DR-1 to afford a DR-1 functionalized PVK in almost complete conversion. The T_g of the resulting polymer is 185 °C, and the orientation behavior of its poled film is studied by UV−visible spectroscopy. The NLO activity, which is estimated to be 20 pm/V by in situ second harmonic generation measurement, remains unchanged at 120 °C for over 1000 h after a minor initial drop.

Introduction

Organic chromophore-containing polymeric materials, represented by electrooptical (E−O) polymers and photorefractive (PR) polymers, are of great interest for potential applications in optoelectronic and photonic technologies.[1] Diverseness of polymer chemistry enables researchers to design and synthesize a variety of polymer systems and then optimize their comprehensive properties for practical application. Over the past several years, high glass transition temperature (T_g) E−O polymers, such as polyimides[2] and polyquinolines,[3] have been employed to improve the long-term thermal stability of the dipole orientation in E−O polymers. However, so far there are a relatively limited number of high T_g polymer systems involved in this area because it is not a trivial task to synthesize chromophore-functionalized monomers, and the processing conditions of most of the high T_g polymers are quite demanding for common NLO chromophores and incompatible with the process of device fabrication.

Therefore, recently a conspicuous tendency in the design and synthesis of NLO polymers is to ultilize postfunctionalization, which allows chromophores to be introduced into reactive precursor polymers without exposure of the chromophores to aggressive polymerization conditions.[4,5] Tripathy et al. reported that an epoxy-based precursor polymer was postfunctionalized by an azo coupling reaction and tricyanovinylation to synthesize a series of NLO polymers with different conjugation lengths and electron acceptors.[6] This post-azo-coupling reaction was similarly performed on poly(amic-acid) and afforded after curing several donor-embedded polyimide EO materials reported by Ma et al.[7] Several more generally applicable postfunctionalization reactions were also developed. According to the Zental' method, NLO chromophores are incorporated by reaction of polymer isocyanates with alkyl hydroxy groups of the chromophores to form a urethane linkage between the polymer main chain and chromophore.[8] Jen et al. reported that aromatic polyimides and polyquinolines containing aryl hydoxyl groups were functionalized with alkyl hydroxyl groups of the chromophores by a Mitsunobu reaction under the catalysis of diethyl azodicarboxylate and triphenylphosphine.[3,9]

Poly(*N*-vinylcarbazole) (PVK) as a well-known photoconductive polymer has been widely used as the host polymer in polymeric PR composites ,[10,11] and its high T_g and good processability make it a good candidate for new high T_g polymers exhibiting multifunctional properties for E−O and PR applications. We have previously reported that chloromethylated PVK was functionalized with Dispersed Red 1 (DR-1) by Williamson ether synthesis.[12] In preparation of chloromethylated PVK utilizing chloromethyl methyl ether and zinc chloride,

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a serious cross-linking reaction occurs because of the higher reactivity of the carbazole ring toward electrophilic substitution. Consequently, the chloromethyl content was rather low in the soluble part of chloromethylated PVK. Moreover, further chromophoric functionalization is not easy to complete, and then it is inevitable that the cross-linking tendency of the residual chloromethyl groups often reduces the storage stability of the final soluble product.

Lately, Zhang et al. have reported that a series of acceptor-substituted *N*-vinylcarbazole chromophore were photocopolymerized with *N*-vinylcarbazole, and the PR properties of these PVK-based polymers were studied.[13,14] While these chromophores are attached to the polymers' main chain without any flexible spacers, thus as a result of restricted internal rotation of PVK,[15] this linkage style does not facilitate sufficent alignment of them for NLO application.

In this paper, two successive postfunctionalization reactions performed on PVK are presented with the aim to develop PVK-based NLO polymers with an elevated degree of the chromophoric functionalization and meliorated processibility. Our strategy is that PVK can be partially formylated by standard Vilsmeier reaction, and these formyl groups with high reactivity will be condensed with cyanoacetylated DR-1 to afford a DR-1 functionalized PVK in almost complete conversion.

Experimental Section

Abbreviations. Formylated poly(*N*-vinylcarbazole) is abbreviated as PVK−CHO, and the condensation product of PVK−CHO with cyanoacetylated DR-1 is abbreviated as PVK−DR1.

Methods. Phosphorus oxychloride was purified by twice distillation. PVK was purchased from Tokyo Kasei, and its weight-averaged molecular weight was estimated to be 1.01 $\times 10^6$ together with a polydispersity of 7.42 by gel permeation chromatography (GPC). All other solvents and reagents were used as received without further purification. The following instrumentations were ultilized for spectroscopic measurement: ^{1}H NMR, JEOL FX90Q; IR, NICOLET FT-IR 170SX; UV−vis, SCHIMADZU 160A. Elemental analysis was performed with a CARLOERBA-1106 microelemental analyzer. Differential scanning calorimetry (DSC) was performed in a Rigaku Thermoflex DSC8131, and thermogravimetric analysis (TGA) was conducted in a Rigaku Thermoflex TG8110 at a heating rate of 10 °C/min.

Preparation of Cyanoacetylated DR-1 (Compound 1). DR-1 (0.73 g, 2.32 mmol), cyanoacetic acid (0.2 g, 2.35 mmol), DCC (0.495 g, 2.40 mmol), and 4-(*N*,*N*-dimethyl)aminopyridine (DMAP) (0.03 g, 0.2 mmol) were dissolved in 20 mL of dry THF and stirred at room temperature for 24 h. The precipitate was filtered out and washed with THF for several times. The solvent of the solution was evaporated under reduced pressure, and then the resulting red solid was washed with 0.5 N hydrochloride acid, diluted aqueous solution of sodium bicarbonate, and water. The crude product was purified by column chromatography using chloroform/ethyl acetate (2:1, v/v) to afford compound **1** as a red powder (0.75 g, 85%). mp 163−164 °C. ^{1}H NMR (CDCl$_3$): δ 8.3 (d, J = 9.0 Hz, ArH, 2H), 7.9 (d, J = 9.0 Hz, ArH, 4H), 6.8 (d, J = 9.0 Hz, ArH, 2H), 4.4 (t, J = 5.9 Hz, $-CO_2CH_2-$, 2H), 3.7 (t, J = 5.9 Hz, $-CO_2CH_2$-CH_2-, 2H), 3.4 (q, J = 7.2 Hz, $-NCH_2-$ and $NCCH_2-$, 4H), 1.2 (t, J = 7.2 Hz, $-CH_2CH_3$, 3H). IR (KBr pellet, cm^{-1}): 2217 (ν_{CN}), 1721 ($\nu_{C=O}$). Calcd for $C_{19}H_{19}N_4O_4$: C, 59.83; H, 5.02; N, 18.37. Found: C, 59.73; H, 4.93; N, 18.29.

Preparation of PVK−CHO. To a mixture of *N*-methylformylanilide (MFA) (1.5 mL, 12 mmol) and phosphorus oxychloride (1.1 mL, 11.9 mmol) was added dropwise a solution of PVK (0.5 g, 2.6 mmol) in DMF (8 mL). The reaction mixture was allowed to stirred at room temperature for 1 h, then heated to 45 °C, and left at this temperature for 48 h. The resulting yellowish solution was filtered and poured into 100 g of crashed ice to afford a yellow solid. This precipitate was collected and washed with an aqueous solution of sodium acetate, water, and methanol. The crude product was purified by reprecipitation from its clear THF solution into methanol and dried in vacuo to afford PVK−CHO as a pale yellow powder. Yield: 0.34 g (∼63%).

Preparation of PVK−DR1. PVK−CHO (0.3 g, ∼0.675 mmol), compound **1** (0.36 g, 0.945 mmol), and piperidine (10 μL) were dissolved in 8 mL of DMF under an argon atmosphere. The reaction mixture was stirred at 40 °C for 30 h and poured into 50 mL of acetonitrile. The resulting red precipitate was collected and purified by reprecipitation from its clear THF solution into acetonitrile. The product was collected and dried in vacuo at 65 °C for 48 h. Yield: 0.3 g.

Polymer Film Preparation. PVK−DR1 was dissolved in NMP and the solution (∼8 wt %) was filtered through syringe filters. Thin polymer films were spin-coated onto an indium tin oxide (ITO) substrate from this solution and dried in vacuo.

Characterization of Poled Films. The second-order optical nonlinearity of PVK−DR1 was determined by in situ second harmonic generation (SHG) experiments. Thus, a closed temperature-controlled oven having optical windows and equipped with three needle electrodes was used. The film, which was kept at 45° to the incident beam, was poled inside the oven, and the SHG intensity was monitored simultaneously. The poling condition was as follows: voltage, 7 kV at the needle point; gap distance, 0.8 cm. The SHG measurements were carried out with a Nd: YAG laser operating with a 10-Hz repetition rate and an 8-ns pulse width at 1064 nm. A Y-cut quartz crystal served as a reference. The NLO coefficient d_{33} was deduced by comparing the intensities of the SHG signals of the poled film with those of the quartz crystal. The dependence of the poling-induced orientation stability on the curing temperature was studied also using this apparatus.

Results and Discussion

As shown in Scheme 1, PVK was partially formylated by the standard Vilsmeier reaction, and PVK−DR1 was synthesized by Knoevenagel condensation between PVK−CHO and compound **1**.

The IR spectra of PVK, PVK−CHO, and PVK−DR1 are shown in Figure 1. In the IR spectrum of PVK−CHO, a strong absorption band is observed near 1687 cm^{-1}, which is in the frequency range expected for the carbonyl stretching vibration of an aromatic aldehyde. After being further functionalized with cyanoacetylated DR-1, this band vanishes and new absorption bands at 1721 and 2218 cm^{-1} emerge, respectively contributed by the carbonyl stretching vibration of a conjugated carboxylic ester and the nitrile stretching vibration; moreover, new absorption bands at 1590 and 1515 cm^{-1} can be attributed to the characteristic peaks of the DR-1 chromophore. All these absorptions are not present in the starting PVK.

The formylation degree of PVK−CHO, which is defined as the molar percentage of the formylated carbazole ring in the PVK long chain, is estimated to be 52% from the comparison of the integration of the aldehyde and carbazolyl aromatic protons, and according to the procedure, PVK can be formylated to different degrees

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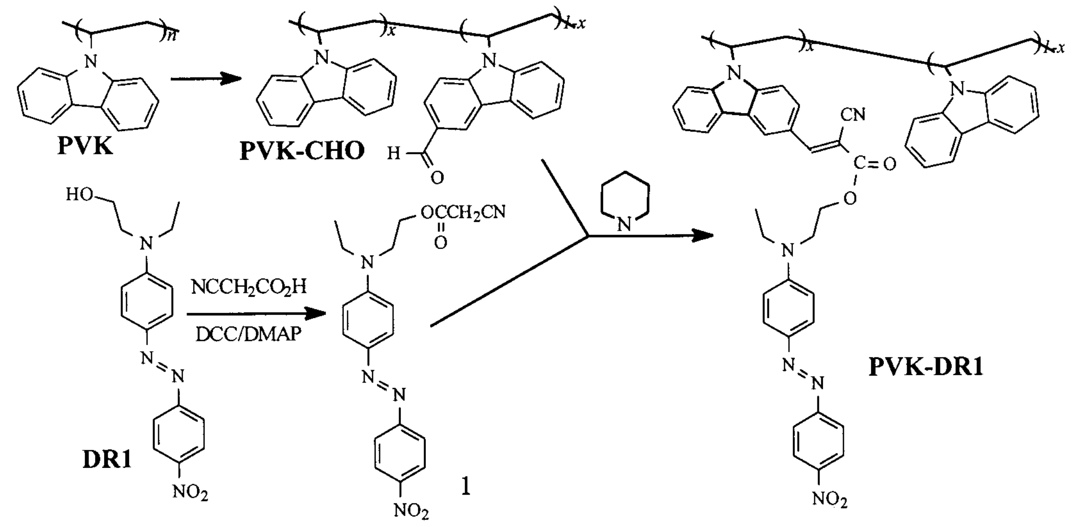
Scheme 1



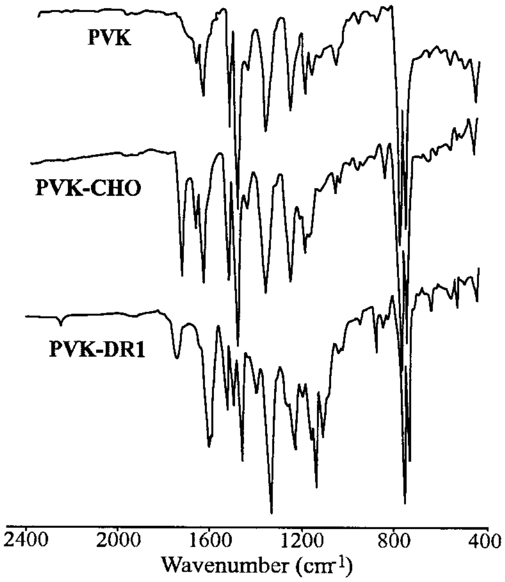


Figure 1. IR spectra of PVK, PVK−CHO, and PVK−DR1.

by modulating the ratio of reagents and the length of the reaction period.

The formyl groups have high reactivity toward Knoevenagel condensation, and the cyanoacetate is selected as the active hydrogen species because of its high reactivity and minimized byproduct in this reaction.[16] The ^{1}H NMR spectrum of PVK−DR1 is shown in Figure 2, in which two peaks assigned to the formyl groups of PVK−CHO disappear. While several new peaks emerge distinctively over the broad band of the spectrum of PVK, these peaks are in good agreement with the chemical shift of the substituted α-cyanoacrylate of DR-1 as shown in Figure 2. Therefore, the formyl groups of PVK−CHO can be condensed with cyanoacetylated DR-1 to afford DR-1-functionalized PVK in almost complete conversion.

The glass transition temperature of PVK−DR1 is determined to be 185 °C by DSC, and thermal stability of PVK−DR1, estimated by TGA, shows that the polymer has good thermal stability up to 277 °C in air.

PVK−DR1 is soluble in common organic solvents, such as THF, $CHCl_3$, DMF, DMSO, and NMP, and a uniform and transparent thin film could be prepared by casting its solution onto an ITO substrate.

The noncentrosymmetric alignment of chromophores, which is essential for second-order optical nonlinearity, is achieved by corona poling, and Figure 3 provides the UV−vis spectra of the polymer film before and after poling. It can be seen that, after poling, the absorbance of the band with the absorption maxima (λ_{max}) at about 470 nm, corresponding to the intramolecular charge transfer of the DR-1 chromophore, decreases significantly. When the absorption spectrum of the THF solution of the poled polymer has also been compared with that of the unpoled one, identical spectra are observed. This evidence demonstrates that the reduction of the absorbance is not due to the decomposition but is due to the dipolar alignment of the DR-1 chromophore, and the order parameter ϕ ($=1 - A_1/A_0$, where A_0 and A_1 are the maximum absorbances before and after poling, respectively) is calculated to be 0.23. However, another strong absorption band with the λ_{max} around 410 nm, which corresponds to the charge transfer of [2-cyano-3-[9-alkyl substituted]carbazolyl]-acrylate chromophore,[17] shows almost the same absorbance before and after poling, indicating that it is very difficult to align this chromophore, even at elevated temperature, by corona poling. As mentioned above, this acceptor-substituted carbazole chromophore is directly attached to the polymer's main chain, so we think that the internal rotation of PVK is restricted too severely to reorientate it. It must be pointed out that even if this carbazole chromophore were efficiently aligned as DR-1 is, the NLO activity of PVK−DR1 should be mainly attributed to the DR-1 chromophore instead of the carbazole chromophore because the $\mu\beta$ value of DR-1 is many times higher than that of the carbazole chromophore.

In situ SHG experiments show that the SHG signals of the poled PVK−DR1 film began to emerge at 165 °C and strengthens quickly thereafter (Figure 4). The SHG intensity reached near-saturation at 180 °C, the tem-

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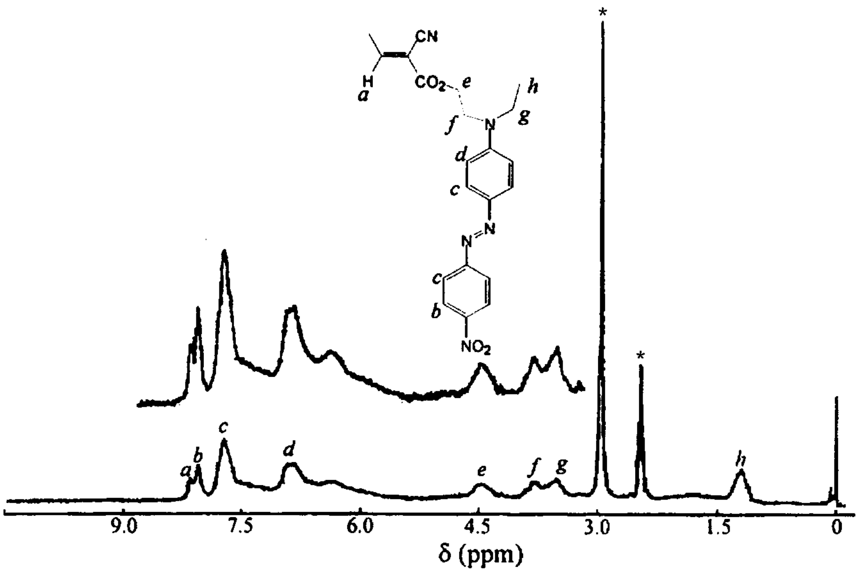

Figure 2. ^{1}H NMR spectrum of PVK−DR1 in DMSO-d_6 (*, solvents) and the assignment of new absorption peaks.

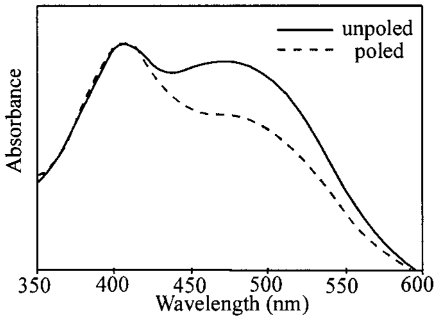

Figure 3. Absorption spectra of unpoled and poled films of PVK−DR1.

perature quite close to the T_g of PVK−DR1. Calculation of the d_{33} value for the poled PVK−DR1 is based upon the equation as shown below,[18]

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

where the $d_{11,q}$ is d_{11} of the quartz crystals, which is 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 polymeric films, and F is the correction factors of the apparatus and equals 1.2 when $l_c \gg l_s$. The d_{33} of the poled PVK−DR1 film is calculated to be 20 pm/V at 1064-nm fundamental wavelength, and by using the approximation two-level model, the nonresonant d_{33} value is estimated to be 3.5 pm/V.

The dynamic thermal stability of the SHG signal was investigated through a depoling experiment in which the real time decay of the SHG signal is monitored as the poled film is heated at a rate of 4−5 °C/min in the range of 35−205 °C. Figure 5 shows that the decay onset of the SHG signals occurred around 150 °C, and the half-decay temperature of the signals is 188 °C. A plot of $d_{33}(t)/d_{33}(0)$ versus time at the temperature of 100 and 120 °C is shown in Figure 6. It can be seen that, after an initial decrease, the SHG signals remained after 1000 h at both temperatures. These thermal characteristics indicate that PVK−DR1, a thermoplastic polymer with good processibility, possesses remarkable stability and could be useful for extensive device exploration.

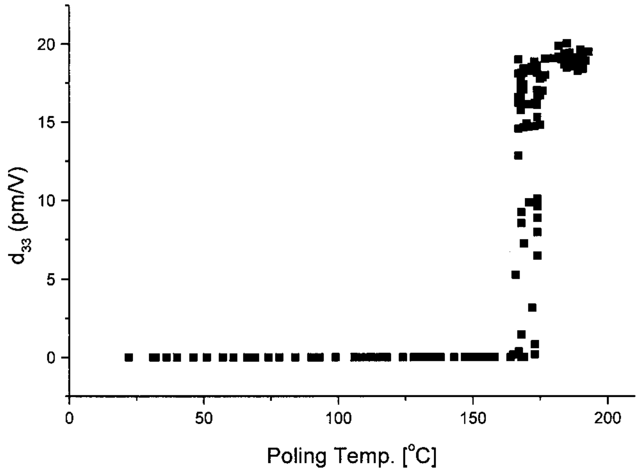

Figure 4. Temperature dependence of the d_{33} value of PVK−DR1 during the process of corona poling.

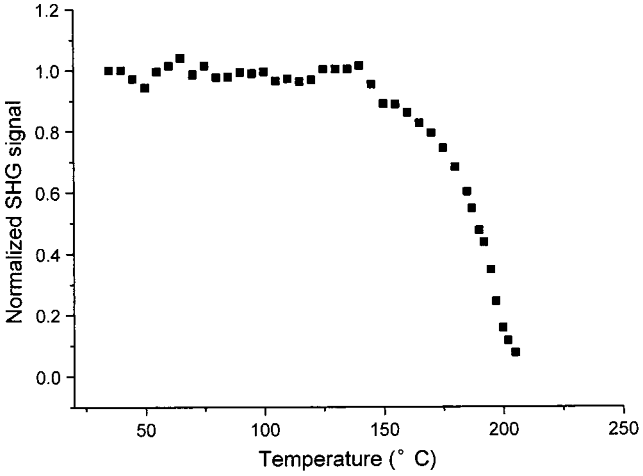

Figure 5. Decay of the SHG coefficient signals as a function of temperature for PVK−DR1.

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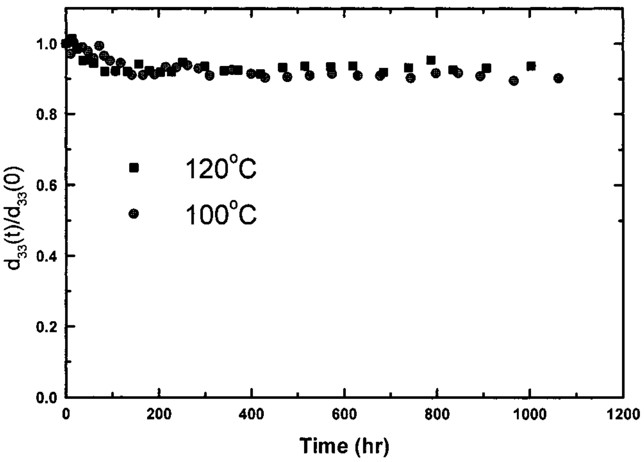

Figure 6. Temporal stability of the normalized SHG coefficient $d_{33}(t)/d_{33}(0)$ of PVK−DR1 at 100 and 120 °C.

On the other hand, there is a possibility that the polymer may also exhibit photoconductivity to some extent. If it is the case, PVK−DR1 should be a potential multifunctional photorefractive polymer. Compared with other carbazole-containing fully functionalized photorefractive polymers,[19−21] PVK−DR1 has a higher T_g and minimized inert components; therefore, a new opportunity has been provided to develop thermally stable second-order NLO polymers with photorefractivity, if any, for long-term holographic data storage.[22]

Conclusion

A new PVK-based polymer with highly functionalized chromophores, high T_g and improved processibility (such as solubility and poling efficiency) was successfully synthesized by two successive postfunctionalizations, and the resulting polymer exhibited thermally stable optical nonlinearity. This polymer is a good candidate for high T_g polymers exhibiting multifunctional properties for electrooptic and photorefractive applications.

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