New Indole-Based Chromophore-Containing Main-Chain Polyurethanes: Architectural Modification of Isolation Group, Enhanced Nonlinear Optical Property, and Improved Optical Transparency

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Three indole-based nonlinear optical (NLO) chromophores with changeable isolation groups were successfully introduced into the polymer backbone to yield a series of main-chain polyurethanes. Thanks to the main-chain structure and the advantages of the indole-based chromophores, all of the polymers show excellent transparency, good processability, thermal stability, and relatively good NLO effects. The obtained experimental results indicated that the polymer backbone, in addition to the linked isolation moieties, could act as isolation spacers in some special cases. The tested NLO results demonstrated that the isolation groups with apparent site-isolation effect might not benefit the macroscopic NLO effect of the resultant polymers.

Introduction

Many reports are concerned with the indole-containing moieties in the literature, because indole is a very important building block for not only naturally occurring compounds, but also lots of synthetic chemicals for different applications.[1] In the indole ring, there are a total of 10 electrons (eight π electrons and one pair of electrons on the nitrogen atom) to form the big π system; however, the electronic cloud does not distribute equally on the nine atoms. In the big π system of indole, there might be not only the electronic properties of π electrons, but also those of n electrons in some degree, especially the electron cloud on the five-membered ring. Thus, this special structural characteristic offers indole moieties good building blocks for new functional materials with interesting electronic or photonic properties, although the related reports are still very scarce.[2]

On the basis of the literature,[2] in the past several years, we have prepared many indole-containing functional materials, which demonstrated exciting phenomena.[3] For example, indole was utilized to build new second-order nonlinear optical (NLO) chromophores as electronic donor groups instead of the general used aniline moieties; interestingly, the indole-based chromophores exhibited comparable or superior nonlinear optical properties in comparison with their aniline-donor analogues, but displayed blue-shifted absorption (even up to 30 nm).[3c] The abnormal results obtained so far in our group were really peculiar and seldom observed, and hence prompted us to prepare more other indole-containing functional materials and study their possibly unique properties.

Very recently, on the basis of the work reported in the literature,[4–9] we have tried to explore some approaches to partially solve one of the major problems encountered in optimizing organic second-order nonlinear optical (NLO) materials: to efficiently translate the large β values of the organic chromophores into high macroscopic NLO activities of polymers,

according to the site-isolation principle.[10] Our research demonstrated that the macroscopic nonlinearity of NLO polymers could be boosted much higher by bonding "suitable isolation groups" onto the NLO chromophore moieties.[11] We applied this concept of "suitable isolation groups" to indole-based materials and designed a series of NLO polyurethanes containing indole-based chromophore moieties, which showed excellent transparency, good processability, thermal stability, and relatively good NLO effects, thanks to the special electronic properties of indole moieties.[12]

Generally, the poling efficiencies and the macro-scale NLO properties of polymers containing dendronized chromophore as side groups are expected to be heavily related to the subtle difference in architectural design.[13] Encouraged by the facts that the same NLO chromophores could lead to different results in different polymer systems after being bonded to different isolation groups,[11] in this Article, we prepared three new indole-based chromophore-containing main-chain polyurethanes (Scheme 1), in which the subtle structure could be modified conveniently. Interestingly, in comparison with its monomer **3**, **P3** exhibited much blue-shifted maximum absorption wavelengths (up to 21 nm) in highly polar solvent such as DMF and NMP, with, however, similar λ_{max}'s in solvents with relatively low polarity, for example, chloroform and dichloromethane. We ascribed the abnormal phenomena to the "site-isolation effect" as reported in the literature.[14] However, in our case, the observed results indicated that the polymer backbone itself should act as "isolation groups" to some degree, and, perhaps, this site-isolation effect caused by the polymer backbone has never been reported yet. In addition, all of the polymers showed good performance and might be good candidates for the practical applications. Herein, we would like to report their syntheses, linear, and nonlinear optical properties in detail.

Experimental Section

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

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SCHEME 1
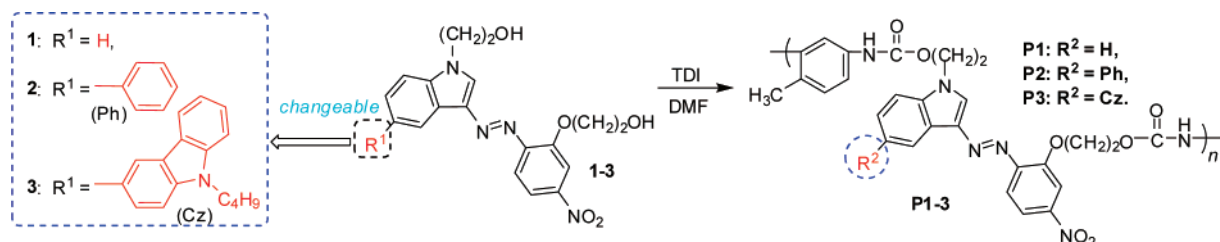
from CaH₂ under an atmosphere of dry nitrogen. 2,4-Toluene-diisocyanate (TDI) was purified by distillation under reduced pressure before use. All other reagents were used as received.

Instrumentation. ^{1}H NMR was conducted with a Varian Mercury300 spectrometer using tetramethylsilane (TMS; δ = 0 ppm) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer-2 spectrometer in the region of 3000−400 cm^{-1} on NaCl pellets. UV−visible spectra were obtained using a Schimadzu 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 an eluent, and the flow rate was 1.0 mL/min. Thermal analysis was performed on a NETZSCH STA449C thermal analyzer at a heating rate of 10 °C/min in argon at a flow rate of 50 cm³/min for thermogravimetric analysis (TGA). The thermal transitions of the polymers were investigated using a METTLER differential scanning calorimeter DSCP200 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.

General Procedure for the Synthesis of Polyurethanes P1−P3. Chromophore **1** or **2** or **3**, and TDI with equivalent molar ratios, were reacted in appropriate anhydrous DMF at 80 °C for about 40 h under an atmosphere of dry nitrogen. After being cooled to ambient temperature, the resultant solution was dropped into methanol to remove monomers. The polymer was filtered and dried in a vacuum desiccator.

P1. Chromophore **1** (208 mg, 0.56 mmol), TDI (97 mg, 0.56 mmol). Red solid (230 mg, 75.4%). M_w = 27 100, M_w/M_n = 1.15 (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 1738 (C=O), 1608 (−C=C−), 1529, 1333 (−NO₂−). ^{1}H NMR (DMSO-d_6) δ (ppm): 9.8−9.6 (−NH−), 9.1−8.9 (−NH−), 8.5 (ArH), 8.0−7.9 (ArH), 7.8−7.6 (ArH), 7.2−7.0 (ArH), 4.6 (−O−CH₂−), 4.3 (−O−CH₂−), 3.9 (−O−CH₂−), 3.8 (−N−CH₂−), 2.2 (−CH₃). UV−vis (THF, 0.02 mg/mL) λ_{max} (nm): 437.

P2. Chromophore **2** (150 mg, 0.34 mmol), TDI (59 mg, 0.34 mmol). Red solid (150 mg, 71.9%). M_w = 22 700, M_w/M_n =

1.13 (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 1728 (C=O), 1598 (−C=C−), 1521, 1327 (−NO₂−). ^{1}H NMR (DMSO-d_6) δ (ppm): 9.8−9.6 (−NH−), 9.1−8.9 (−NH−), 8.8−8.6 (ArH), 8.0−7.9 (ArH), 7.7 (ArH), 7.5 (ArH), 7.0 (ArH), 4.6 (−O−CH₂−), 4.3 (−O−CH₂−), 3.9 (−O−CH₂−), 3.8 (−N−CH₂−), 2.2 (−CH₃). UV−vis (THF, 0.02 mg/mL) λ_{max} (nm): 443.

P3. Chromophore **3** (155 mg, 0.26 mmol), TDI (46 mg, 0.26 mmol). Red solid (120 mg, 59.8%). M_w = 16 300, M_w/M_n = 1.13 (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 1734 (C=O), 1602 (−C=C−), 1525, 1333 (−NO₂−). ^{1}H NMR (DMSO-d_6) δ (ppm): 9.8−9.6 (−NH−), 9.1−8.9 (−NH−), 8.5−8.2 (ArH), 7.9−7.5 (ArH), 7.1−7.0 (ArH), 4.6−4.3 (−O−CH₂− and −N−CH₂−), 3.9−3.7 (−O−CH₂− and −N−CH₂−), 2.2 (−CH₃), 1.7 (−CH₂−), 1.2 (−CH₂−), 0.8 (−CH₃). UV−vis (THF, 0.02 mg/mL) λ_{max} (nm): 442.

Preparation of Polymer Thin Films. The polymers were dissolved in DMF (concentration ∼3 wt %), and the solutions were filtered through syringe filters. Polymer films were drop-coated onto indium−tin−oxide (ITO)-coated glass substrates, which were cleaned by *N,N*-dimethylformide, acetone, distilled water, and THF sequentially in an ultrasonic bath before use. Residual solvent was removed by heating the films in a vacuum oven at 40 °C.

NLO Measurement of Poled Films. The second-order optical nonlinearity of the polymers was determined by an in-situ second harmonic generation (SHG) experiment using a closed temperature-controlled oven with optical windows and three needle electrodes. The films were kept at 45° to the incident beam and poled inside the oven, and the SHG intensity was monitored simultaneously. Poling conditions were as follows: temperature, different for each polymer (Table 1); voltage, 7.5 kV at the needle point; gap distance, 0.8 cm. The SHG measurements were carried out with a Nd:YAG laser operating at a 10 Hz repetition rate and an 8 ns pulse width at 1064 nm. A Y-cut quartz crystal served as the reference.

Results and Discussion

Synthesis. The synthetic route of chromophores is shown in Scheme S1, while that of polymers is shown in Scheme 1. Under the normal azo coupling reaction conditions, chromophores **1**

TABLE 1: Some Characterization Data of Polymers

no.	yield %	$M_w{}^a$	$M_w/M_n{}^a$	$\lambda_{max}{}^b$ (nm)	$T_g{}^c$ (°C)	$T_d{}^d$ (°C)	$T_e{}^e$ (°C)	$l_s{}^f$ (μm)	$d_{33}{}^g$ (pm/V)	$d_{33(\infty)}{}^h$ (pm/V)	Φ^i
P1	75.4	27 100	1.15	437 (432)	150	261	154	0.45	51.2	13.8	0.09
P2	71.9	22 700	1.13	443 (437)	165	258	160	0.54	54.1	13.7	0.11
P3	59.8	16 300	1.13	442 (451)	160	258	180	0.55	35.0	9.0	0.12

^{a} Determined by GPC in DMF on the basis of a polystyrene calibration. ^{b} The maximum absorption wavelength of polymer solutions in THF, while the maximum absorption wavelength of the corresponding small chromophore molecules in diluted THF solutions is given in the parentheses. ^{c} Glass transition temperature (T_g) of polymers detected by the DSC analyses under nitrogen at a heating rate of 10 °C/min. ^{d} The 5% weight loss temperature of polymers detected by the TGA analyses under argon at a heating rate of 10 °C/min. ^{e} The best poling temperature. ^{f} Film thickness. ^{g} Second harmonic generation (SHG) coefficient. ^{h} The nonresonant d_{33} values calculated by using the approximate two-level model. ^{i} Order parameter $\Phi = 1 - A_1/A_0$; A_1 and A_0 are the absorbances of the polymer film after and before corona poling, respectively.
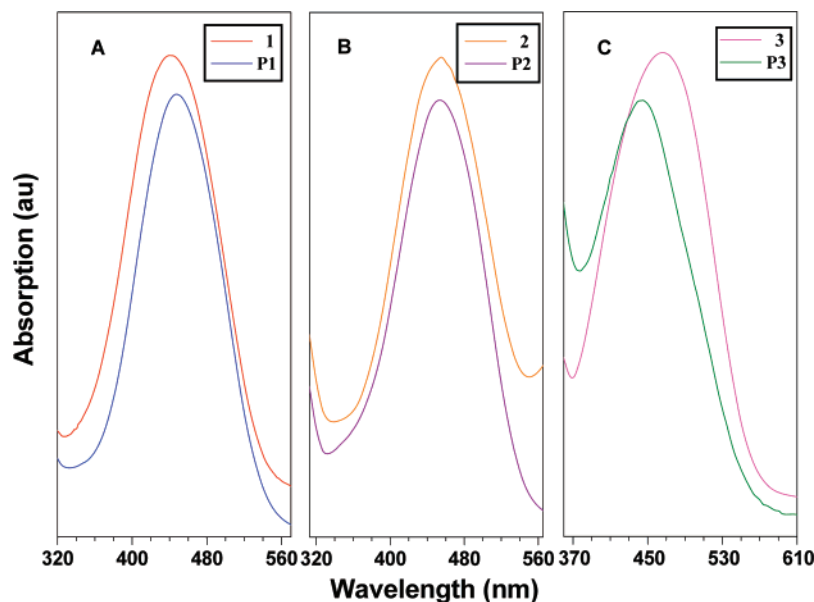
Figure 1. UV−vis spectra of NMP solutions of (A) chromophores **1** and **P1**, (B) chromophores **2** and **P2**, and (C) chromophores **3** and **P3**.

and S**4** were easily obtained, and the latter one underwent the followed Suzuki reactions to afford chromophores **2** and **3** conveniently. Thus, chromophores **1**−**3** possessed similar push−pull structure, but different isolation groups, changing from hydrogen atoms to carbazolyl groups. The main-chain polyurethanes, **P1**−**3**, were easily obtained from the corresponding chromophores and TDI under conditions similar to those reported in the literature.[15] As there were nearly no different reactivities between the two hydroxyl groups in the chromophores, it was expected that the chromophore dipoles should be randomly arranged in the polymer backbone as reported in the literature and our previous case.[11e,12] Also, this structure would benefit the alignment of chromophore moieties upon poling.

Structural Characterization. All of the polymers were characterized by spectroscopic methods and gave satisfactory spectral data (see Experimental Section, Supporting Information and Table 1 for detailed analysis data). In the IR spectra of chromophores and polymers, there was a strong absorption peak centered at about 1330 cm^{-1}, which should be ascribed to the signal of nitro groups. Another strong absorption peak appeared at about 1734 cm^{-1} in **P1**−**P3**, which was attributed to the vibration of the carbonyl group in a urethane group, indicating the formation of urethane linkages during the polymerization process as shown in Scheme 1.[15] In all of the ^{1}H NMR spectra of the polymers **P1**−**P3**, the chemical shifts were consistent with the proposed polymer structure as demonstrated in Scheme 1, however, showing an inclination of signal broadening due to polymerization. For example, Figure S1 showed the spectra of chromophore **2** and the corresponding polymer **P2**. It was obvious that there were some small peaks present in the down fields besides those signals derived from the chromophore moieties. These peaks were assigned to the urethane unit formed in the polymerization process,[15] further confirming the successful polymerization between chromophore **2** and TDI.

The molecular weights of polymers were determined by gel permeation chromatography (GPC) with DMF as eluent, and polystyrene standards as calibration standards. All of the results were summarized in Table 1. The polymers were thermally stable, their TGA thermograms were shown in Figure S2, and the 5% weight loss temperatures of polymers are listed in Table 1. The glass transition temperatures (T_g) of the polymers were

TABLE 2: The Maximum Absorption Wavelength (nm) of Chromophores and Polymers in Different Solvents

	CHCl$_3$	dichloromethane	THF	DMF	NMP
1	431	433	432	439	440
P1	440	436	437	445	446
2	441	440	437	448	453
P2	443	442	443	451	453
3	442	446	451	465	465
P3	443	440	442	448	444

investigated using a differential scanning calorimeter (Table 1), and polymers generally have relatively high T_g above 150 °C due to the strong secondary forces between polymer chains and the main-chain structure.

UV−Vis Spectra and Site-Isolation Effects. All of the polymers were soluble in common polar organic solvents such as DMF and DMSO. The UV−vis absorption spectra of the chromophores and polymers in NMP were demonstrated in Figure 1, while their maximum absorption wavelengths (λ_{max}) in THF are shown in Table 1. It was easily seen that the chromophore moieties in **P1** and **P2** exhibited red-shifted maximum absorption (about 5 nm) in comparison with those of the free chromophores in THF (Table 1), while that of **P3** blue-shifted 9 nm in the same solvent. As shown in Figure 1, this phenomenon was more obvious when NMP was used instead of THF: the λ_{max} of **P1** was red-shifted 6 nm in comparison with that of chromophore **1**, while **P2** demonstrated nearly the same λ_{max} as chromophore **2**. However, the difference between the λ_{max}'s of **P3** and chromophore **3** was as large as 21 nm. This indicated that the λ_{max} of chromophores and polymers had a strong reliance on the solvents. Thus, we further measured their UV−vis spectra (Figures S3−S8) in different solvents, with the results summarized in Table 2.

Generally, **P1** and **P2** exhibited red-shifted or similar λ_{max} values in comparison with chromophores **1** and **2**, respectively. In chloroform, the same phenomenon was observed in the UV−vis spectra of **P3** (443 nm) and chromophore **3** (442 nm). However, in other solvents, the difference between **P3** and chromophore **3** became larger, from 6 nm in dichloromethane to 21 nm in NMP. The abnormal results of **P3** should surely be caused by its different structure from those of **P1** and **P2**. As discussed in the synthetic part, different isolation groups could be conveniently linked to the chromophore moieties in polymers,
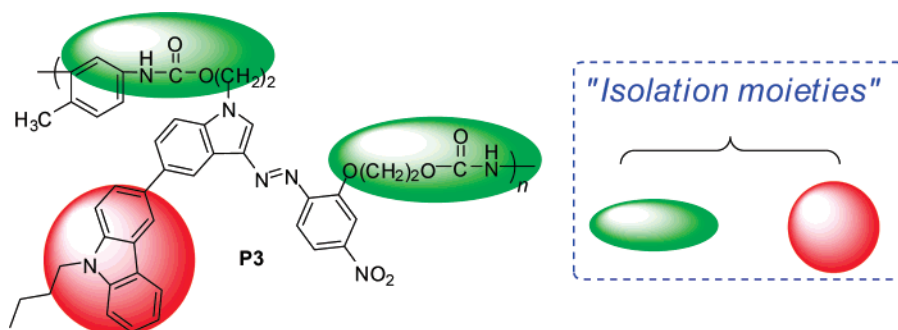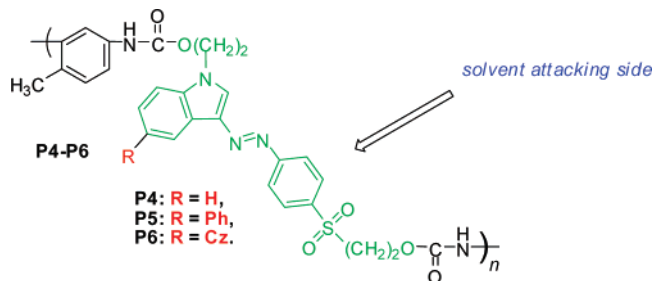
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CHART 1

CHART 2

TABLE 3: The Maximum Absorption Wavelength (nm) of Polymers P4−P6 in Different Solvents

	CHCl₃[a]	dichloromethane	THF	DMF	NMP
P4	393 (395)	392 (394)	392 (395)	395 (397)	397 (400)
P5	399 (401)	397 (399)	401 (398)	401 (403)	399 (403)
P6	398 (397)	397 (397)	398 (398)	397 (400)	402 (405)

[a] The maximum absorption wavelength of the corresponding small chromophore molecules in diluted solutions is given in the parentheses.

and from **P1** to **P3**, the isolation spacer became larger. After the isolation groups were bonded, the environment of the push−pull chromophore moieties was different. The effective site isolation could be achieved to reduce the aggregation between chromophore moieties, and the site-isolation effect could be indicated by the UV−vis spectra.[14] Thus, the abnormal UV−vis absorption behavior of **P3** should disclose that the chromophore moieties in it were surrounded by the isolation groups, which shielded the chromophore moieties from the solvatochromic effect. As the isolation groups in **P1** and **P2** were much smaller than the carbazolyl moieties in **P3**, it was reasonable that no obvious site-isolation effect was observed in their UV−vis spectra. As to the free molecule of chromophore **3**, the large carbazolyl groups could not protect the donor−acceptor chromophore structure from the interaction with the solvent molecules, or, in another word, in **P3**, not only the introduced isolation groups (Cz), but also the formed polymer backbone could shield the push−pull structure. Thus, perhaps, we could say that in the case of **P3**, the polymer backbone was the isolation moiety in some degree, and the speculated cartoon picture might be as that shown in Chart 1.

Previously, we have prepared three other polymers **P4−P6**, with their structures (Chart 2) similar to those of **P1−P3**.[12] Encouraged by the results obtained in the UV−vis spectra of **P1−P3**, we also studied the optical behavior of **P4−P6**. As shown in Table 3, the maximum absorption wavelengths of polymers were similar to their corresponding chromophores in the same solvents. Comparing the structures of **P1−P3** with those of **P4−P6**, there were two different points: one was the different acceptor group, and another was the different linkage points in the polymer backbone. The latter should account for

their different absorption behavior. Thus, our obtained results demonstrated that the subtle structure could affect the macroscopic properties of the polymers in a large degree. Therefore, it might be an alternative route to modify the property of the resultant polymers by just changing the linkage model of the functional moieties during the construction process of the polymers.

It should be pointed out that if not the indole groups but aniline ones were used as the donor in the chromophore moieties, the maximum absorptions should be longer than 490 nm, more than 50 nm red-shifted in comparison with our results reported here.[3] This point reminded us of the special electronic property of indole moieties and would result in the low optical loss of the polymers. For example, Figure S9 exhibited the UV−vis spectra of chromophore **1** and its analogue with aniline moieties as donor group (**S7**, Chart S1). It was easily seen that the λ_{max} of chromophore **1** was blue-shifted about 66 nm, in comparison with that of chromophore **S7**. Thus, the much blue-shifted maximum absorption of the chromophore moieties would lead to the good, even excellent optical transparency of the resultant polymers, due to the less optical loss at the operation wavelength of electro-optical devices (typically 0.8, 1.3, and 1.5 μm).[9]

NLO Properties. To evaluate the NLO activity of the polymers, their poled thin films were prepared. The most 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. To check the reproducibility of the results, we repeated the measurements several times for each sample. The method for the calculation of the SHG coefficients (d_{33}) for the poled films has been reported in our previous papers.[3,11,12] From the experimental data, the d_{33} values of **P1−P3** were calculated at 1064 nm fundamental wavelength (Table 1). With different isolation groups, the three polymers exhibited different NLO properties. In comparison with **P4−P6**, **P1−P3** demonstrated much higher NLO effects, because nitro groups are stronger acceptors than sulfonyl ones.

To show the NLO results more visually, we compared the d_{33} values of the polymers using that of **P1** as reference (Figure 2A). It was seen that **P2** exhibited a d_{33} value similar to that of **P1**; however, the data of **P3** decreased sharply, although the apparent "site-isolation effect" was observed in their UV−vis spectra. However, on the other hand, the introduction of different isolation groups would surely lead to the different molar weights of the obtained chromophores, which resulted in the diluted concentration of the active chromophore moieties in the polymer. According to the one-dimensional rigid orientation gas model:[16]

$$d_{33} = \frac{1}{2} N\beta f^{2\omega} (f^{\omega})^2 \langle \cos^3 \theta \rangle \qquad (1)$$
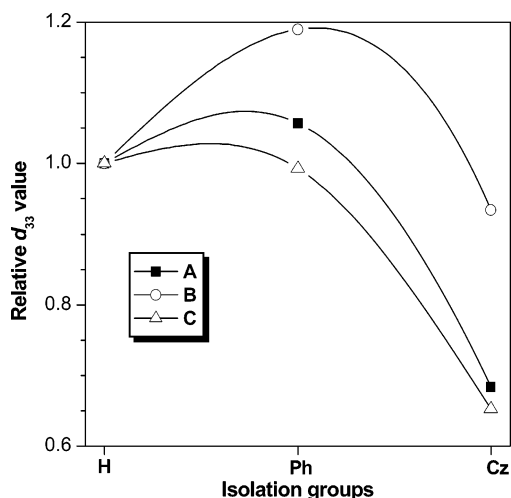
Figure 2. (A) The comparison of the d_{33} values of the polymers, (B) the comparison of the calculated d_{33} values, which were obtained by using the tested d_{33} values dividing the concentration of the active chromophore moieties of the polymers, and (C) the comparison of the calculated $d_{33(\infty)}$ values according to the approximate two-level model, using **P1** as reference.

where N is the number density of the chromophore, β is its first hyperpolarizability, f is the local field factor, 2ω is the double frequency of the laser, ω is its fundamental frequency, and $\langle \cos^3 \theta \rangle$ is the average orientation factor of the poled film, we compared their NLO results again, using the tested d_{33} values dividing the concentration of the active chromophore moieties (the basic push−pull part of the chromophore moieties in the structure of the polymers as shown in Scheme 1) in the polymers, with that of **P1** still as reference (Figure 2B). The trend of this curve was similar to that of curve A, but there were some different points. After the linkage of the phenyl groups, the NLO effect of **P2** was boosted to about 1.2 times that of **P1**, but in curve A, the difference between them was not so obvious, indicating that the introduction of the isolation groups really diluted the concentration of the active chromophore moieties. This influence could also be observed in the case of **P3**: if the concentration of the active chormophore moieties was considered, as shown in curve B, **P3** exhibited an NLO effect similar to that of **P1**; however, the tested data of **P3** were much lower than those of **P1**. This phenomenon further proved the three impacts caused by the introduced isolation groups: (1) to minimize the strong intermolecular dipole−dipole interactions to some degree, leading to the improvement of the d_{33} values of the polymers as many scientists expected; (2) to dilute the active concentration of the chromophore moieties, generally reducing the d_{33} values; and (3) to increase the bulk of the resultant chromophore moieties, making the noncentrosymmetric alignment of the chromophore upon poling in the electronic field more difficult, which would generate complicated effects on the resultant d_{33} values (at the beginning, the enlargement of the size would benefit the alignment due to the minimized electrostatic interaction, but would restrain the alignment when the size is too bulky).

Thus, really, affected by these three main impacts, there was a suitable isolation group present to boost the fixed microscopic β value of chromophore moieties to possibly higher macroscopic NLO property efficiently. Here, for the indole-based chromophore with nitro acceptors, the suitable isolation group was phenyl moieties. As discussed in the UV−vis spectra, the different isolation groups resulted in the minor difference of the maximum absorption wavelength (λ_{max}) of these three

polymers. Thus, if deducting the resonant enhancement caused by the absorption of the chromophore moieties at 532 nm by using the approximate two-level model, the NLO properties of **P1**−**P3** should be smaller as shown in Table 1 ($d_{33(\infty)}$). Curve C in Figure 2 demonstrated the results with **P1** as reference; its trend was nearly the same as that of curve A, because the three polymers exhibited similar λ_{max}.

Therefore, despite the apparent "site-isolation effect" in **P3**, the carbazolyl moieties were not the suitable isolation groups for the indole-based chromophore reported here. This fact might indicate that the isolation group with the observed apparent site-isolation effect would not ensure that: (1) it was the suitable isolation group to boost the fixed microscopic β value of chromophore moieties to possibly higher macroscopic NLO property efficiently; and (2) it could benefit the macroscopic NLO property of the polymers. That is to say, the linkage of this isolation group might decrease the macroscopic NLO property of the resultant polymers, just like the case of **P3**, due to the diluted concentration of the active chromophore moieties.

Thus, the macroscale NLO properties of polymers containing chromophores with isolation groups were expected to be heavily related to the subtle difference in architectural design. The examples presented here demonstrated the importance of the polymer structure and the negative effect of the site-isolation effect. So, it was very important to rationally design the subtle structure of the NLO polymer containing the fixed chromophore moieties to achieve a possibly higher macroscropic NLO effect by applying the site-isolation principle.

Conclusions

In summary, three new main-chain polyurethanes (**P1**−**P3**) containing indole-based chromophores were prepared. All of the polymers were well characterized, and the preliminary results demonstrated the following points:

(1) For the first time, indicated by the UV−vis spectra, the polymer backbone was observed to act as the isolation moieties to lead to the site-isolation effect.

(2) The presence of the site-isolation effect could be negative to the macroscopic NLO effect of the resultant polymers.

(3) All of the polymers exhibit excellent transparency, good processability, thermal stability, and relatively good NLO effects, thanks to the special electronic properties of indole moieties. Thus, they could be promising candidates for practical application in the photonic fields.

Therefore, our study may provide useful information for the design of new NLO polymers with the aim to boost the fixed microscopic β value of chromophore moieties to possibly higher macroscopic NLO property efficiently in polymers. Further study is still in progress in our lab.

Supporting Information Available: Detailed synthetic procedures and characterization data for the monomers, figures of TGA and UV−vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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