Synthesis and characterization of main-chain, second-order, nonlinear optical polyurethanes with isolation moieties and zigzag structures

Ying Li, Ting Yu, Zuojia Li, Zhenguo Wang, Qiang Peng

Key Laboratory of Green Chemistry and Technology of the Ministry of Education, College of Chemistry, and State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610064, People's Republic of China
Correspondence to: Q. Peng (E-mail: qiangpengjohnny@yahoo.com)

ABSTRACT: In this study, two main-chain second-order nonlinear optical (NLO) polyurethanes were successfully prepared with indole-based chromophores. The introduced phenyl isolation group and the continuous zigzag polymer backbone were found to be helpful for effectively decreasing the intermolecular dipole–dipole interactions and enhancing the NLO properties of the resulting polymers. The studied polymers exhibited good optical transparency, high thermal stability, and excellent NLO effects; this indicated that the nonlinearity–stability trade-off and nonlinearity–transparency trade-off could be alleviated by this newly designed polymer system. Poly{4-anilinocarbonyl[N-ethoxyl-5-phenyl-3-azo(2′-oxyethylene-4′-nitrobenzene)indole]carbonylimino} with a zigzag backbone showed a large second harmonic generation coefficient (d_{33}) value of 88.4 pm/V. However, poly{5-naphthyliminocarbonyl[N-ethoxyl-5-phenyl-3-azo(2′-oxyethylene-4′-nitrobenzene)indole]carbonylimino} (PUAZN) with a continuous zigzag structure exhibited a higher d_{33} value of 116.2 pm/V, which was attributed to the unique rigid and zigzag linkage of 1,5-naphthalene as the isolation spacer. The enhanced NLO efficiency and relatively longer term temporal stability made PUAZN as a promising candidate for practical applications in photonic devices. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42974.

INTRODUCTION

In past decades, organic second-order nonlinear optical (NLO) materials have attracted wide interest for their potential applications in high-speed electrooptic modulators, optical switches, and frequency converters.[1–14] Compared to the commercial lithium niobate (LiNbO$_3$), polymeric NLO materials possessed a lot of advantages, including a large NLO effect, low cost, fast response time, high bandwidth, small driving voltage, and easy device fabrication.[13–16] To meet the requirements of the practical applications, NLO polymers should have a large macroscopic optical nonlinearity, high physical and chemical stability, and good optical transparency.[15,16] However, the efficient translation of the large first hyperpolarizabilitiy (β) values of the organic chromophores into highly macroscopic polymeric NLO activities is still a challenge. The reason is that the organic chromophore moieties in their polymeric system process very strong intermolecular dipole–dipole interactions; these can cause a poling-induced noncentrosymmetric alignment.[17,18] In the early time, Jen, Dalton, and coworkers[15–19] proposed the site-isolation principle, which was proven to be an efficient approach for minimizing these interactions and enhancing the poling efficiency. On the basis of this principle, many chromo-

phore structures have been designed and synthesized from linear structures to L-shaped, X-shaped, H-shaped, and star-shaped structures to improve their topological structures.[20–29]

Among these topologies, H-shaped NLO materials have been studied widely. In 2006, Li et al.[30] reported the first H-type chromophore and its polyurethane materials, which exhibited enhanced NLO effects in comparison with their linear analogs. In 2008, Lu and coworkers[31,32] also synthesized a series of NLO polymers embedded with H-type chromophores; they proved that the H-type chromophore could be an effective method to solve the nonlinearity–transparency trade-off. Dendritic NLO materials with a three-dimensional spherical shape, including hyperbranched polymers, dendronized polymers, and dendrimers, have been discovered to be another excellent molecular topology for constructing highly efficient NLO materials.[15,33–35] Li and coworkers[30,36–38] introduced suitable isolation groups onto the chromophore skeletons in dendronized polymers, and the macroscopic nonlinearity was increased several times. The same group prepared a new series of NLO dendrimers though a double-stage method with a click chemistry reaction. The tested second harmonic generation coefficient (d_{33}) value reached 193.1 pm/V; this was still the highest value reported so far for
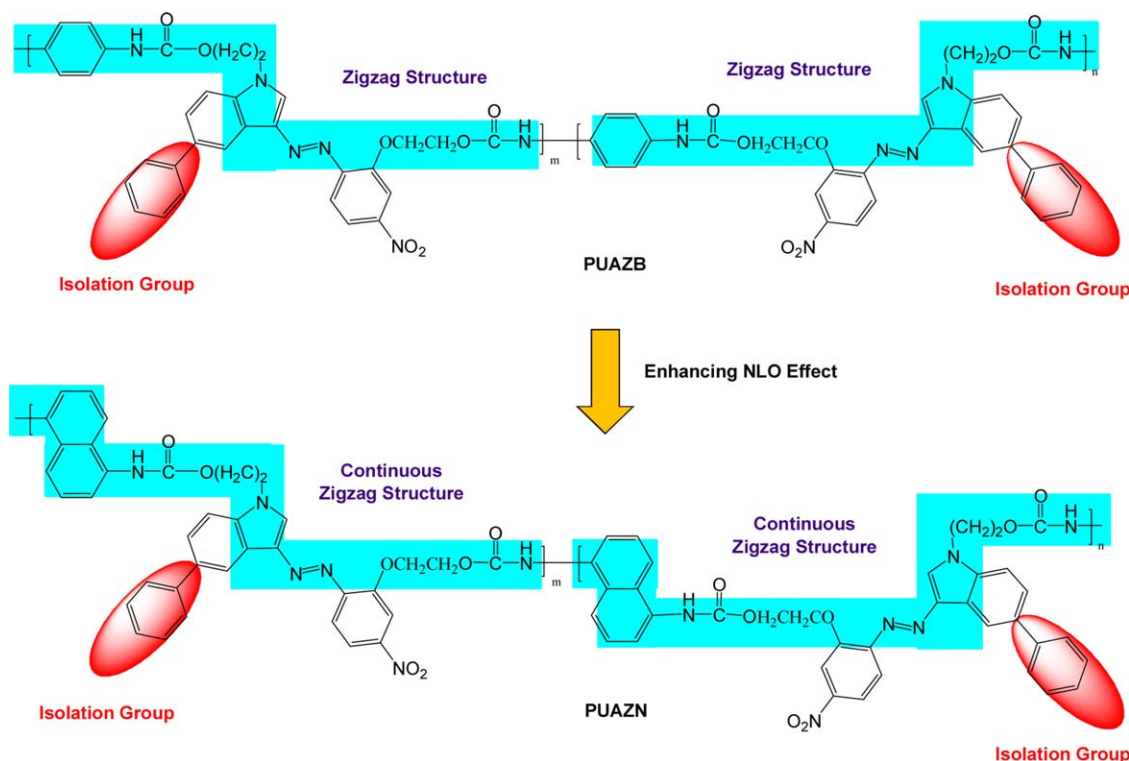
Scheme 1. Structures of the NLO polyurethanes and design concept of this study. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

simple azo chromophore moieties.[39,40] In 2007, with the self-assembly of aromatic/perfluoroaromatic dendron-substituted chromophore moieties through the presence of complementary Ar–ArF supramolecular interactions, Jen and coworkers[41,42] developed a new kind of molecular glass with improved poling efficiency and macroscopic NLO effects. Recently, Li et al.[43] used two methods of Ar–ArF self-assembly and isolation chromophores to design and synthesize a series of NLO dendrimers; they exhibited a very large efficiency up to a new record highest value of 257 pm/V for simple azo chromophore moieties.

From the reported literature, we observed that most work has focused on the control of the shape of the chromophores and the designation of different isolation chromophores. However, few studies have been devoted to the adjustment of the chemical bond linkage of the designed NLO activities and the polymeric hosts, despite dendrimers and their analogs. Because of the synthetic complexity of the dendritic structures, it is important to explore this nonlinear linkage effect on the NLO efficiency of second-order nonlinear polymers containing NLO chromophores on the polymer main chains with simple synthetic procedures. In this study, we designed and prepared two main-chain NLO copolymers, poly{4-anilinocarbonyl[N-ethoxyl-5-phenyl-3-azo(2′-oxyethylene-4′-nitrobenzene)indole]carbonylimino} (PUAZB) and poly{5-naphthyliminocarbonyl[N-ethoxyl-5-phenyl-3-azo(2′-oxyethylene-4′-nitrobenzene)indole]carbonylimino} (PUAZN), with different zigzag structures (Scheme 1); these were expected to decrease the intermolecular dipole–dipole interactions and enhance the NLO efficiency of the resulting polymers. Polyurethanes were chosen here as the polymer backbone because they

could form extensive hydrogen bonding between urethane linkages and increase the rigidity to prevent the relaxation of the induced dipoles.[44–48] On the other hand, the azo chromophores with nitro moieties were used as the NLO active moieties in this study because of their easy obtainment and wide usage in second-order NLO materials and devices.[3,49–52] The introduction of the isolation group of the benzene unit to the azo chromophore moieties dramatically improved the NLO effect of the resulting polymeric materials by further weakening the strong intermolecular dipole–dipole interactions between the highly polar azobenzene chromophore moieties in the polymeric system; this has been well described in previous literature.[53,54] So, here we report the synthesis, characterization, and optical nonlinearities of these two NLO polymers in detail.

EXPERIMENTAL

Materials and Instrumentation

All chemicals were purchased in reagent-grade form from Aladdin, Adamas, Aldrich, and Alfa Chemical Co. and were used without further purification. All solvents were dried and freshly distilled immediately before use. The chromophore of N-hydroxyethyl-5-phenyl-3-azo(2′-hydroxyethoxy-4′-nitrobenzene) indole (IAZ) was prepared according to literature methods.[53] The NMR spectra were measured on a Bruker ARX 400 NMR spectrometer with dimethyl sulfoxide (DMSO) as the solvent and tetramethylsilane as the internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 560 spectrometer on NaBr pellets. The molecular weights of the copolymers were determined by gel permeation chromatography (GPC) analysis (Waters 1515) with dimethylformamide (DMF) as the eluent and polystyrene as the

Table I. NLO Properties of the Polymers

Polymer	T_p (°C)[a]	l_s (μm)[b]	d_{33} (pm/V)	$d_{33,t}$ (pm/V)[c]	N[d]	Φ[e]
PUAZB	155	0.45	88.4	21.9	0.56	0.15
PUAZN	165	0.50	116.2	27.1	0.52	0.20

[a] Best poling temperature.
[b] Film thickness.
[c] Calculated with the approximate two-level model.
[d] Active chromophore moiety loading density.
[e] $\Phi = 1 - A_1/A_0$, where A_1 and A_0 are the absorbances of the polymer film after and before corona poling, respectively.

standard. Ultraviolet–visible (UV–vis) spectra were obtained with a Carry 300 spectrophotometer. Thermogravimetric analysis (TGA) was conducted on a TA Instruments model SDT Q600 simultaneous TGA/differential scanning calorimetry (DSC) analyzer at a heating rate of 10°C/min under an N_2 flow rate of 90 mL/min. The thickness of the films was measured with a Dektak 6 M surface profilometer.

General Procedure for the Synthesis of the Polymers

The chromophore IAZ and 1,4-benzene diisocyanate or 1,5-naphthalene diisocyanate with equivalent molar ratios were reacted in appropriate anhydrous DMF at 80°C for about 48 h under dry nitrogen protection. After it was cooled to room temperature, the resulting solution was dropped slowly into methanol and precipitated to afford the crude product. The process was repeated several times to remove the unreacted monomers. The polymer was finally collected by filtration and dried *in vacuo*.

Polymer PUAZB

Chromophore IAZ (0.2410 g, 0.54 mmol) and 1,4-benzene diisocyanate (0.0864 g, 0.54 mmol) were used to produce PUAZB, which was obtained as a red solid (0.1450 mg, 45.8%).

Weight-average molecular weight (M_w) = 28,300. M_w/number-average molecular weight (M_n) = 1.28. ^{1}H-NMR [400 MHz, hexadeuterated dimethyl sulfoxide (DMSO-d_6), δ, ppm]: 9.70–9.47 (d, 1H), 8.59–8.48 (m, 2H), 8.03–7.35 (m, 11H), 4.59 (m,8H). FTIR spectroscopy(KBr pellet, cm^{-1}): 3229.16, 1711.53, 1635.97, 1516.59, 1406.65, 1328.49, 1215.05, 1074.95, 831.04, 757.80, 520.68. UV–vis spectroscopy [tetrahydrofuran (THF), maximum absorption wavelength (λ_{max}), nm]: 440. ANAL. Calcd for $(C_{32}H_{26}N_6O_7)_n$: C, 63.36%; H, 4.32%; N, 13.05%. Found: C, 62.02%; H, 4.10%; N, 13.28%.

Polymer PUAZN

The chromophore IAZ (0.2410 g, 0.54 mmol) and 1,5-naphthalene diisocyanate (0.1135 g, 0.54 mmol) were used to obtain PUAZN as a red solid (0.1676 mg, 47.3%).

M_w = 22,500, M_w/M_n = 1.22. ^{1}H-NMR (400 MHz, DMSO-d_6, δ, ppm): 9.69–9.61 (m, 2H), 8.84–8.50 (m, 2H), 8.06–7.93 (m, 3H), 7.91–7.62 (m, 6H), 7.62–7.19 (m, 7H), 4.88–4.26 (m, 8H). FTIR spectroscopy (KBr pellet, cm^{-1}): 3382, 3282, 3109, 3066, 2949, 1720, 1631, 1600, 1524, 1473, 1424, 1371, 1329, 1221, 1160, 1080, 963, 893, 867, 806, 771, 698, 581. UV–vis spectroscopy (THF, λ_{max}, nm): 442. ANAL. Calcd for $(C_{36}H_{28}N_6O_7)_n$: C, 65.85%; H, 4.30%; N, 12.80%. Found: C, 64.15%; H, 4.03%; N, 12.61%.

Preparation of the Polymer Thin Films

The resulting polymers were first dissolved in dry DMF with a concentration of 3 wt %, and the solutions were then filtered through syringe filters. Polymer thin films were coated onto indium tin oxide (ITO) glass plates by a wet-process method; they were cleaned sequentially by acetone, distilled water, DMF, and THF in an ultrasonic bath. The residual solvent was finally removed by the heating of the prepared polymer films in a vacuum oven at about 40°C.

NLO Measurement of the Poled Polymer Films

The second-order optical nonlinearity of the polymers was evaluated by an *in situ* second harmonic generation (SHG) experiment. The samples were put into a closed temperature-controlled oven with optical windows and three needle electrodes. The studied films were kept at 45° to the incident beam and poled inside the oven, and the SHG intensity was monitored at the same time. The poling conditions were as follows: temperature, see Table I; voltage = 7.7 kV at the needlepoint; and gap distance = 0.8 cm. The SHG experiments were performed with an Nd:YAG laser operating at a 10-Hz repetition rate and an 8-ns pulse width at 1064 nm. A quartz crystal was used as the reference.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Polymers

The molecular structures of the NLO polymer (PUAZB and PUAZN) and detailed synthetic routes are presented in Schemes 1 and 2. The chromophore IAZ was synthesized under normal azo coupling reaction conditions according to previous literature.[54] The two polyurethanes, PUAZB and PUAZN, were synthesized with the chromophore IAZ and 1,4-phenylene diisocyanate or 1,5-naphthalene diisocyanate under conditions similar to those reported in the literature for the preparation of polyurethanes.[44–48,53,54] Because there were no other different reactivities between the two hydroxyl groups in the IAZ skeleton, the chromophore dipoles were randomly arranged in the polymer main chains; this was helpful for the alignment of IAZ moieties in the poling process.[44–48,53,54] As reported previously,[28] the isolation groups bonded onto the H-type chromophore moieties constructed the dendronlike structures. In this study, our designed polymers, with a continuous zigzag structure and attached suitable isolation groups, could also be expected as a new polymer structure to promote the orientation alignment during the process of corona poling.

The structures of the resulting polymers were confirmed by IR spectroscopy, NMR, and elemental analysis. The IR and ^{1}H-NMR spectra are described in Figure 1. As shown in Figure 1(a), there was a strong absorption peak centered at about 1517 and 1328 cm^{-1}; this was ascribed to the signal of nitro groups. After the chromophore IAZ was copolymerized with diisocyanate derivatives, the absorption bands of the nitro groups still remained in the IR spectra of PUAZB and PUAZN. Another strong absorption peak appeared at about 1715 cm^{-1} in PUAZB and PUAZN; this was attributed to the vibrations of the carbonyl group in a urethane group. This indicated the successful formation of urethane linkages during the polymerization process.[28] The ^{1}H-NMR spectra of PUAZB and PUAZN are presented in Figure 1(b). The
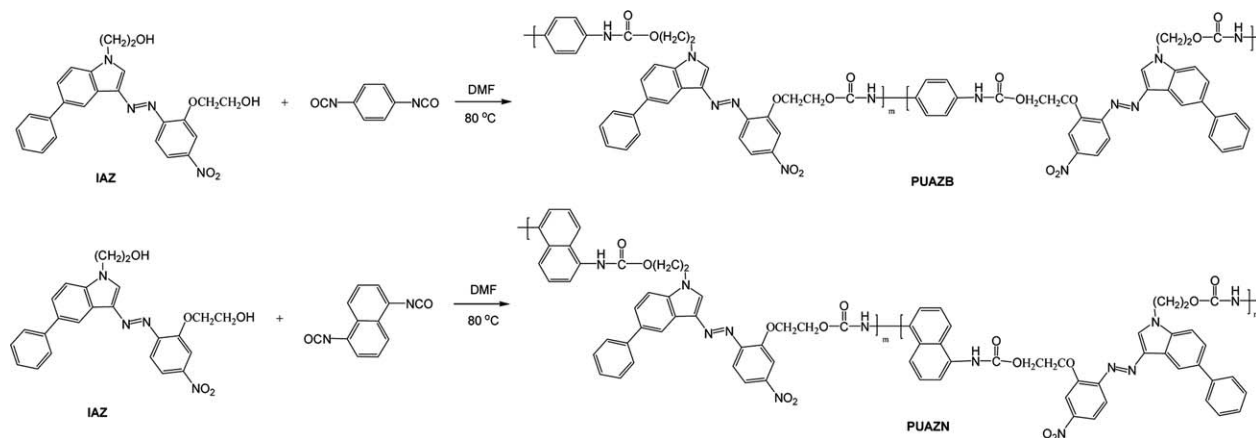
Scheme 2. Synthetic routes of the NLO polyurethanes.
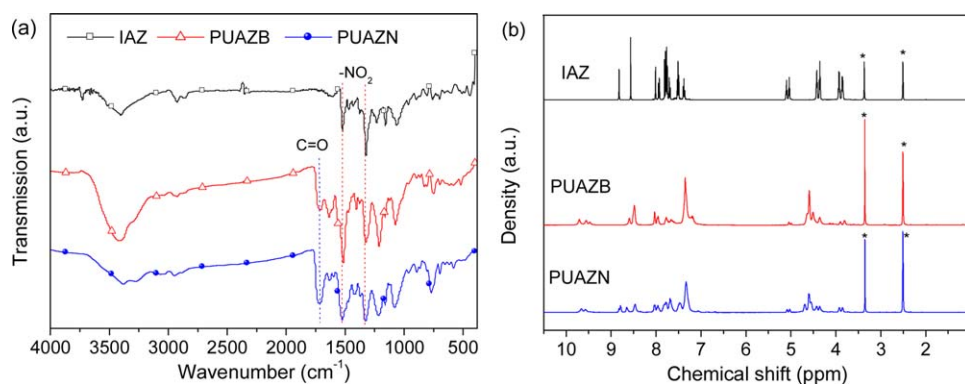
Figure 1. (a) IR and (b) ¹H-NMR spectra of the chromophore IAZ, polymer PUAZB, and polymer PUAZN. The solvent peaks are marked with asterisks. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chemical shifts were consistent with the structures of the resulting polymers, as demonstrated in Scheme 1. An inclination of signal broadening was clearly observed after polymerization. From the spectra of the polymers, there were some small peaks present in the down fields in addition to those signals derived from the IAZ chromophore moieties. These small peaks were associated with the urethane unit formed in the polymerization process[28,53]; this confirmed again the successful polymerization between the IAZ chromophore and the diisocyanate monomers.

The molecular weights (M_w) and polydispersity index (M_w/M_n) of the resulting copolymers were determined by GPC with monodisperse polystyrenes as standards and DMF as an eluent. Both polymers possessed closed molecular weights; this was helpful for making a clear comparison of their properties. The thermal properties were investigated by DSC and TGA, which were shown in Figure 2a and 2b. The decomposition onset temperature values (ca. 5% weight loss) were determined by TGA to be 168 and 211°C for PUAZB and PUAZN, respectively. The thermal
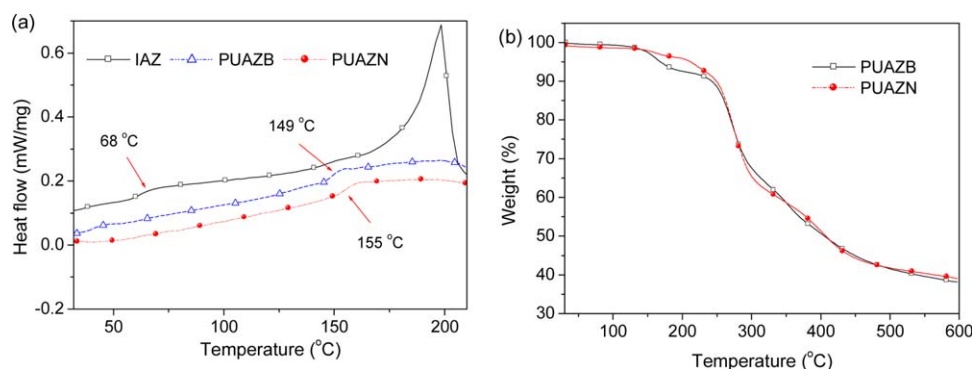
Figure 2. (a) DSC and (b) TGA curves of PUAZB and PUAZN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Molecular Weights and Thermal and Optical Properties of the Polymers

Polymer	Yield (%)	M_w (kDa)[a]	Polydispersity index[a]	T_g (°C)[b]	T_d (°C)[c]	λ_{max} (nm)[d]
PUAZB	45.8	28,300	1.28	149	168	440
PUAZN	47.3	22,500	1.22	155	211	442

[a] Molecular weights and polydispersity indices were determined by GPC in DMF with polystyrene as the standard.
[b] Detected by DSC analysis under nitrogen at a heating rate of 10°C/min.
[c] Onset decomposition temperature (5% weight loss) detected by TGA under N_2 at a heating rate of 10°C/min.
[d] λ_{max} of polymer solutions in THF.

stabilities of these copolymers were adequately suitable for their applications in NLO applications. PUAZN exhibited better thermal stability than PUAZB; this was attributed to the incorporation of naphthalene groups in the main chains. The glass-transition temperature (T_g) of the polymers were investigated with DSC measurements in the range 0–210°C from the second heating and cooling runs. Small-molecule IAZ exhibited a melting point at about 198°C. However, this type of endothermic peak disappeared for its polymers. PUAZB exhibited an obscure T_g at 149°C, whereas PUAZN had an obvious T_g at 155°C. The relatively high T_g value of PUAZN was also attributed to the introduction of naphthalene groups; this enhanced the rigidity of the polymer backbone. IAZ also showed a T_g at 68°C; this was much lower than those of the corresponding polymers. After the small molecule was polymerized, the movement was limited by the polymeric backbone; this resulted in higher T_g values in its poly-

mers. The results of molecular weights and the thermal analysis are summarized in Table II.

UV–Vis Spectra

All of the polymers were easily soluble in common polar organic solvents, such as DMF, DMSO, N-methyl-2-pyrrolidone (NMP), and THF. Their solutions were easily spin-coated into solid films; therefore, it was convenient to evaluate their NLO properties with the thin films later. The UV–vis absorption spectra of the chromophore IAZ and the polymers PUAZB and PUAZN in different solvents are shown in Figure 3, and the λ_{max} values for the π–π^* transitions of their azo chromophores are listed in Table III. After they were bonded to the polymer chain, it was easy to see that the maximum absorptions of the IAZ chromophore of PUAZB and PUAZN were blueshifted compared with those of the free IAZ molecules. This blueshifted maximum absorption would surely afford the wide optical transparency window for their practical applications.[43,55,56] This change indicated that electronic interactions existed between the chromophore moieties and the polymer chain.[44–48] Previous work[28,54] showed that the blueshift of the linear polymers containing IAZ could be up to 19 nm in a THF solution. However, the blueshifted extent of PUAZB and PUAZN in this study showed a reduced blueshift (<5 nm in THF). After naphthalene was used instead of a benzene skeleton, PUAZN showed a smaller blueshift compared with PUAZB. Obviously, the continuous zigzag structure in PUAZN caused by the covalent linkage of the 1,5 position of naphthalene efficiently reduced the aggregation of the chromophores. This weakened the interaction of the chromophore moieties and polymer main chains; this was of great benefit in improving the NLO properties of the related polymers. This was also confirmed by the UV–vis absorption of
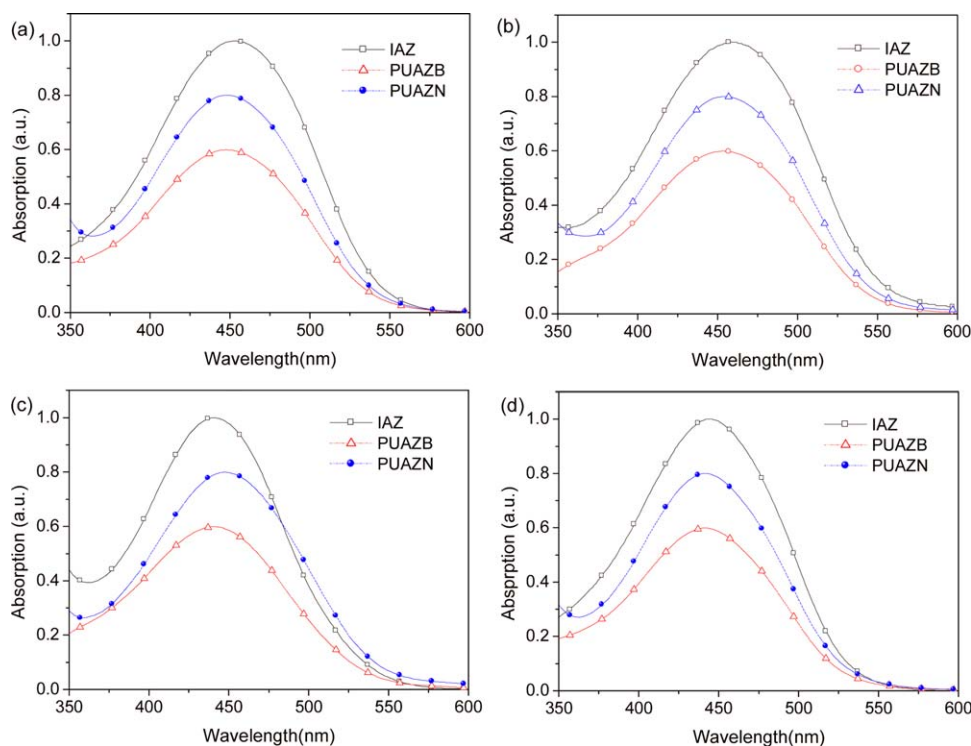
Figure 3. UV–vis spectra of the (a) DMF, (b) DMSO, (c) NMP, and (d) THF solutions of the chromophore IAZ, polymer PUAZB, and polymer PUAZN (0.02 mg/mL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. λ_{max} (nm) Values of Chromophores and Polymers

	DMF	DMSO	NMP	THF	Film
IAZ	453	460	441	446	—
PUAZB	447	453	442	441	443
PUAZN	448	456	447	442	444

The concentrations of the chromophore and polymer solutions were fixed at 1.0×10^{-5} mol/mL and 0.02 mg/mL, respectively.

their thin films. As shown in Figure 4, from solution to the solid state, the absorption peaks of the PUAZB and PUAZN films were redshifted to about 443 and 444 nm, respectively. Because the small molecule of IAZ showed very poor film formation ability, we did not obtain its UV–vis absorption. Obviously, the slight redshifts signified a small aggregation of the chromophores and polymer backbones even in the solid state; this was different from those of the conjugated polymers.[57] The reason was that the introduced amide and alkoxyl bonds cut off the conjugation of the polymer main chains.

NLO Properties

To study the NLO properties of the resulting polymers, the related poled thin films were prepared by the wet-process method. We repeated the measurements several times for each sample to guarantee the reproducibility of the measurements. It is known that the simple and convenient characterization of the second-order NLO activity is the determination of the NLO coefficient (d_{33}), which was calculated from the following equation:

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

where $d_{33,s}$ is the NLO coefficient of the sample; $d_{11,q}$ is the NLO coefficient of the quartz crystals, which is equal to 0.45 pm/V; I_s and I_q are the SHG intensities of the sample film and quartz plate, respectively; $l_{c,q}$ is the coherent length of the quartz plate; l_s is the thickness of the sample film; and F is the correction factor of the apparatus, which was equal to 1.2 when $l_c \gg l_s$. The d_{33} values of the PUAZB and PUAZN films were calculated at a fundamental wavelength of 1064 nm. The poling and measurement conditions were taken according to previous literature,[28,54] and the obtained results are summarized in Table I.

The primary results indicate that both polymers showed large macroscopic NLO activities. PUAZB exhibited a d_{33} value of 88.4 pm/V. However, PUAZN showed a higher d_{33} value of 116.2 pm/V; this was about 1.3 times that of PUAZB. Considering the nearly same loading densities of the effective chromophore (0.56 for PUAZB and 0.52 for PUAZN), the unique continuous zigzag structures introduced in PUAZN were responsible for this improvement of the poling efficiency. Although the chromophore IAZ in these two polymers contained an isolation group of benzene, the 1,5-naphthalene in PUAZN backbone was a rigid skeleton that acted as another isolation group to minimize the strong dipole–dipole interactions among the high polar chromophore moieties in this polymer system to enhance its NLO effect. Thus, the use of rigid and continuous zigzag structures of polymer backbones might be a good strategy for solving this challenge in the field of NLO research: how to efficiently translate the large β values of the small molecular chromophores into high macroscopic NLO activities of their polymers.

As there might be some resonant enhancement caused by the absorption of the chromophore moieties at 532 nm, the NLO properties of PUAZB and PUAZN [Nonresonant NLO coefficient value ($d_{33}(\infty)$)] should be smaller if these enhancement sections are deducted (Table III); these values were calculated with an approximate two-level model. Because of the high d_{33} value and the improved optical transparency, the $d_{33}(\infty)$ values of PUAZB and PUAZN were 21.9 and 27.1 pm/V, respectively. Actually, both polymers exhibited higher $d_{33}(\infty)$ values than those of the reported linear NLO polymers, especially main-chain polymers, which bore similar active chromophore moieties.

To further study the alignment behavior of the IAZ moieties in the polymers, the order parameter (Φ) of the polymers was also measured and calculated from the change in the UV–vis spectra of their films before and after corona poling under an electric field, according to the equation described in Table I (footnote e). Figure 4 shows the UV–vis spectra of the films of PUAZB and PUAZN before and after the corona poling processes. Obviously, the dipole moments of the chromophore moieties in the polymers were aligned, and the absorption intensities decreased because of birefringence after poling. The tested Φ values were in good accordance with their d_{33} values; these are compared in Table I. Both polymers exhibited higher Φ values than those of the reported linear polymers; this indicated the good alignment of
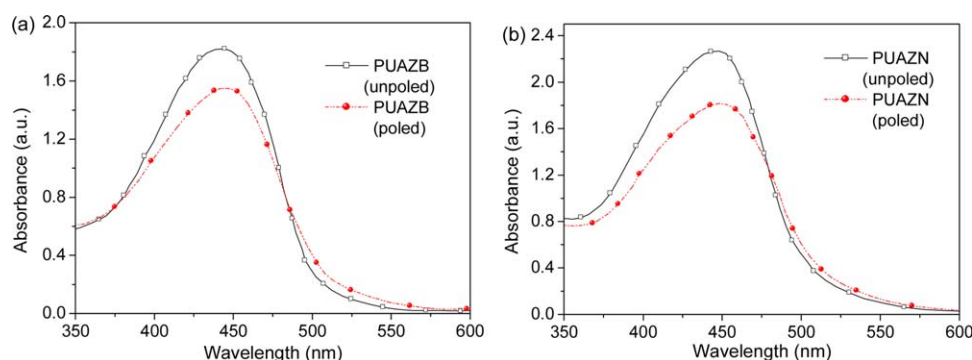
Figure 4. UV–vis absorption spectra of (a) PUAZB and (b) PUAZN before and after poling. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
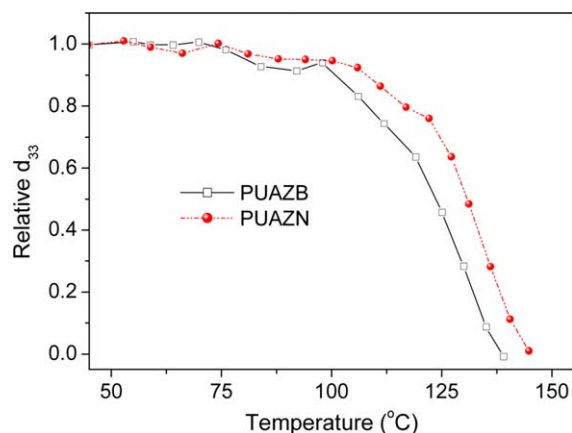
Figure 5. Decay curves of the d_{33} values of PUAZB and PUAZN as a function of the temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chromophore (IAZ) moieties in the designed zigzag polymer system. As expected, PUAZN showed a higher Φ value (0.20) than that (0.15) of PUAZB. This confirmed that the effectively oriented alignment of the dipole moments was obtained in the former polymer. The reason was attributed to the effect of the isolation chromophore. Because the IAZ isolation group was the same, 1,5-naphthalene afforded a rigid and continuously zigzag structure and acted as the second isolation units in the main chains. This helped IAZ to be isolated well and increase the d_{33} value; this was similar to the previously reported results with a second isolation chromophore to enhance Φ and the NLO properties.[58–60]

The dynamic thermal stabilities of the NLO activities of PUAZB and PUAZN were investigated by the depoling experiments, in which the real-time decays of their SHG signals were monitored as the poled films were heated from room temperature to 145°C in air at a rate of 4°C/min. Figure 5 shows the decay of the d_{33} values of PUAZB and PUAZN as a function of the temperature. As shown in Figure 5, the onset temperatures for decay in the d_{33} values of PUAZB and PUAZN were found to be 108 and 119°C, respectively. Compared with PUAZB, PUAZ exhibited a longer term temporal stability; this makes it a good candidate for practical NLO applications.

CONCLUSIONS

A new type of main-chain NLO copolymers (PUAZB and PUAZN) containing indole-based chromophores (IAZ) were successfully prepared and characterized. The newly designed rigid and zigzag polymer backbones effectively decreased the intermolecular dipole–dipole interactions and enhanced the NLO efficiency of the resulting polymers. These two polymers exhibited good optical transparency, thermal stability, and excellent NLO effects; this indicated that the nonlinearity–stability trade-off and nonlinearity–transparency tradeoff[61–63] were alleviated in our polymer system. PUAZN with 1,5-naphthalene as an isolation spacer had a more continuous zigzag structure than PUAZB with 1,4-benzene; this made the former polymer show enhanced NLO properties and relatively better long-term temporal stability. The high d_{33} value of 116.2 pm/V was obtained

for PUAZN; this suggested promising applications for it in practical photonic fields.

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