Dendronlike Main-Chain Nonlinear Optical (NLO) Polyurethanes Constructed from "H"-Type Chromophores: Synthesis and NLO Properties

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ABSTRACT For the first time, a series of dendronlike main-chain polyurethanes have been successfully designed and synthesized, in which different isolation groups with different sizes were introduced to modify the subtle structure of the used "H"-type chromophores, according the concept of "suitable isolation groups". Thanks to the advantages of "H"-type chromophores and the introduced suitable isolation group, all of the polymers demonstrated large NLO effects, good processability, improved optical transparency, and thermal stability. The obtained experimental results indicated that the utilization of "H"-type chromophores might be a promising choice to efficiently translate the large β values of the organic chromophores into high macroscopic NLO activities of polymers.

KEYWORDS: "H"-type chromophore • nonlinear optics • polyurethane • synthesis • dendronlike structure • suitable isolation groups

INTRODUCTION

Considerable attention has been paid to the second-order nonlinear optical (NLO) polymeric materials because of their huge potential applications in photonics and many advantages over conventional inorganic crystalline materials, such as large nonlinearity, good processability, ultrafast response time, and superior chemical flexibility (1−3). Generally, to exhibit an electrooptical effect, the active moieties, so-called NLO chromophores, with the structure of a donor−π−acceptor, should be poled under an electric field to form a highly ordered noncentrosymmetric alignment (4). Also, in most of the NLO polymers, the chromophore moieties have a linear structure, which leads to strong intermolecular dipole−dipole interactions in the polymeric system and makes the poling-induced noncentrosymmetric alignment of chromophores a daunting task. This fact results in one of the major problems encountered in optimizing organic NLO materials: how to efficiently translate the large β values of the organic chromophores into high macroscopic NLO activities of polymers (5). Actually, in the past decades, thanks to the great efforts of scientists, the β values of chromophores have been improved by up to 250-fold; however, the NLO properties of the polymers are only enhanced several times (6). Fortunately, the work of Jen, Dalton, and co-workers has demonstrated that controlling the shape of chromophores through the introduction of isolation groups could be an efficient method for reducing the interaction and enhancing the poling efficiency to increase the macroscopic NLO effects (7, 8).

In 2006, for the first time, we designed and synthesized a new type of chromophores, termed as "H"-type chromophores, in which the two donor−acceptor blocks were linked together through an isolation group, and the resultant polyurethanes embedded with this "H"-type chromophore (Chart S1 in the Supporting Information) exhibited enhanced NLO effects, in comparison with their linear analogues (9a). Also, we took advantage of the indole groups to construct "H"-type chromophores (Chart S2 in the Supporting Information), which also displayed good performance (9b). The recent results of Lu et al. further confirmed that the usage of "H"-type chromophores could be an effective method for solving the nonlinearity−transparency trade-off (10). Also from 2006, based on the literatures and according to the site-isolation principle (1−3, 5−8, 11), with an attempt to partially dissolve the above challenge (to efficiently translate the large β values of the organic chromophores into high macroscopic NLO activities of polymers), we prepared different kinds of NLO polymers, in which the size of the isolation groups in NLO chromophore moieties was changed from small to larger, and the obtained experimental results demonstrated that the macroscopic nonlinearity of NLO polymers could be boosted several times higher by bonding "suitable isolation groups" to the NLO chromophore moieties (9, 12, 13). Thus, we wondered if some isolation groups were
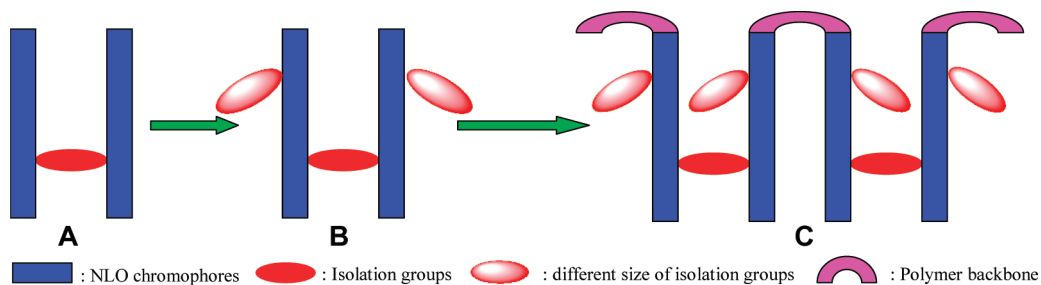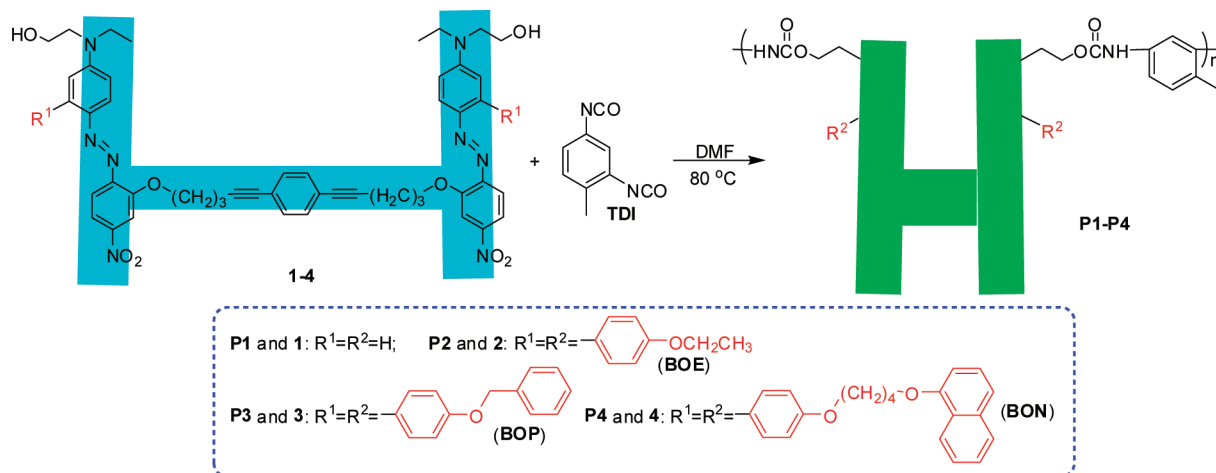
FIGURE 1. Graphical illustration of the dendronlike structure.

Scheme 1

introduced to the "H"-type chromophores, the NLO effects of the resultant polymers might be further increased. However, no related work has been reported.

Therefore, in this paper, a series of polyurethanes embedded with "H"-type chromophores were successfully prepared (Scheme 1), in which the subtle structure were further adjusted, by application of the principle of "suitable isolation groups". As shown in Figure 1 (from A to B), while different sizes of isolation groups were introduced, "H"-type chromophores would form a dendronlike shape. Then, after these dendronlike chromophores underwent a polymerization process (Figure 1C), it was easily seen that the chromophores in the polymeric system were well encapsulated, with almost every position of the chromophores (at the donor side, in the π bridge near the donor side, in the π bridge near the acceptor side, etc.) possessing an isolation group to depress the dipole—dipole interactions. To the best of our knowledge, there were no reports concerned on these kinds of NLO polymers, which could be termed as dendronlike main-chain polymers, in addition to other types of main-chain polymers (head-to-head, tail-to-tail, head-to-tail, etc.) (14). All of the obtained polymers were soluble in common solvents and exhibited good thermal stability and film-forming ability. Interestingly, the apparent isolation effect could be observed from these polymers, and all of the polymers demonstrated large second harmonic generation (SHG) coefficients (up to 127.7 pm/V of **P2**), which should be attributed to their special structure (dendronlike main chain). Also, the order parameter of **P2** was 1.3 times higher than that of **P1**, confirming our above theory. Herein, we

report the synthesis, characterization, and NLO properties of these polymers.

EXPERIMENTAL SECTION

Materials and Instrumentation. *N,N*-Dimethylformamide (DMF) was dried over and distilled from CaH₂ under an atmosphere of dry nitrogen. 2,4-Toluenediisocyanate (TDI) was purified by distillation under reduced pressure before use. ¹H NMR spectra were measured on a Varian Mercury 300 spectrometer using tetramethylsilane ($\delta = 0$ ppm) as the 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—vis spectra were obtained using a Schimadzu UV-2550 spectrometer. Gel permeation chromatography (GPC) was used to determine the molecular weights of the 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 nitrogen at a flow rate of 50 cm³/min for thermogravimetric analysis (TGA). The thermal transitions of the polymers were investigated using a Mettler DSC822e differential scanning calorimeter under nitrogen at a scanning rate of 10 °C/min. The thickness of the films was measured with an Ambios Technology XP-2 profilometer.

General Procedure for the Synthesis of Polyurethanes P1—P4. "H"-type chromophore (**1**—**4**) and TDI with equivalent molar ratios were reacted in an appropriate anhydrous DMF solution at 80 °C for 30—36 h in an atmosphere of dry nitrogen. After the solution was cooled to ambient temperature, it was dropped into methanol to remove the monomer. The polymer was filtered and dried in a vacuum desiccator.

Table 1. Polymerization Results and Characterization Data

no.	yield (%)	$M_w{}^a \times 10^4$	$M_w/M_n{}^a$	$T_g{}^b$ (°C)	$T_d{}^c$ (°C)	$T_e{}^d$ (°C)	$l_s{}^e$ (μm)	$d_{33}{}^f$ (pm/V)	$T_0{}^g$ (°C)	$d_{33}(\infty)^h$ (pm/V)	Φ^i
P1	80.7	1.68	1.27	88	250	100	0.38	118.6	j	14.9	0.20
P2	83.3	2.18	1.29	115	267	121	0.28	127.7	90	15.3	0.26
P3	90.3	2.12	1.24	112	260	122	0.31	108.1	83	13.0	0.22
P4	90.2	2.28	1.31	80	220	95	0.38	83.5	j	10.5	0.14

^{a} Determined by GPC in DMF on the basis of polystyrene calibrations. ^{b} Glass transition temperature (T_g) of polymers detected by DSC analyses under nitrogen at a heating rate of 10 °C/min. ^{c} The 5% weight loss temperature of polymers detected by TGA analyses under nitrogen at a heating rate of 10 °C/min. ^{d} The best poling temperature. ^{e} Film thickness. ^{f} SHG coefficient. ^{g} The onset temperature. ^{h} The nonresonant d_{33} values calculated by using the approximate two-level model. ^{i} Order parameter $\Phi = 1 - A_1/A_0$, where A_1 and A_0 are the absorbances of the polymer film after and before corona poling, respectively. ^{j} Not obtained.

P1: **1** (71 mg, 0.080 mmol), TDI (15 mg, 0.080 mmol). **P1** was obtained as a deep-red powder (69 mg, 80.7%). $M_w =$ 16 800, $M_w/M_n = 1.27$ (GPC, polystyrene calibration). IR (thin film): ν (cm^{-1}) 1727 (C=O), 1513, 1337 ($-$NO$_2$). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.1$-$1.4 ($-$CH$_3$), 2.0$-$2.3 ($-$CH$_2-$ and $-$CH$_3$), 2.6$-$2.8 ($-$CH$_2$C$-$), 3.4$-$4.0 ($-$NCH$_2-$ and $-$OCH$_2-$), 4.2$-$4.4 ($-$OCH$_2-$), 6.7$-$6.9 (ArH), 7.0 (ArH), 7.26 (ArH), 7.6$-$7.8 (ArH), 7.8$-$8.0 (ArH). UV$-$vis (THF, 0.02 mg/mL): λ_{max} (nm) 488.

P2: **2** (83 mg, 0.075 mmol), TDI (14 mg, 0.075 mmol). **P2** was obtained as a deep-red powder (80 mg, 83.3%). $M_w =$ 21 800, $M_w/M_n = 1.29$ (GPC, polystyrene calibration). IR (thin film): ν (cm^{-1}) 1730 (C=O), 1512, 1339 ($-$NO$_2$). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.1$-$1.5 ($-$CH$_3$), 2.1$-$2.4 ($-$CH$_2-$ and $-$CH$_3$), 2.6$-$2.8 ($-$CH$_2$C$-$), 3.4$-$4.0 ($-$NCH$_2-$ and $-$OCH$_2-$), 4.0$-$4.2 ($-$OCH$_2-$), 4.2$-$4.4 ($-$OCH$_2-$), 6.6$-$7.0 (ArH), 7.1$-$7.6 (ArH), 7.6$-$8.0 (ArH). UV$-$vis (THF, 0.02 mg/mL): λ_{max} (nm) 492.

P3: **3** (80 mg, 0.065 mmol), TDI (12 mg, 0.066 mmol). **P3** was obtained as a deep-red powder (83 mg, 90.3%). $M_w =$ 21 200, $M_w/M_n = 1.24$ (GPC, polystyrene calibration). IR (thin film): ν (cm^{-1}) 1730 (C=O), 1516, 1340 ($-$NO$_2$). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.1$-$1.3 ($-$CH$_3$), 2.0$-$2.4 ($-$CH$_2-$ and $-$CH$_3$), 2.6$-$2.8 ($-$CH$_2$C$-$), 3.4$-$4.0 ($-$NCH$_2-$ and $-$OCH$_2-$), 5.0$-$5.2 ($-$OCH$_2-$), 6.6$-$6.9 (ArH), 7.0 (ArH), 7.1$-$7.6 (ArH), 7.6$-$8.0 (ArH). UV$-$vis (THF, 0.02 mg/mL): λ_{max} (nm) 492.

P4: **4** (64 mg, 0.044 mmol), TDI (8 mg, 0.044 mmol). **P4** was obtained as a deep-red powder (65 mg, 90.2%). $M_w = 22\,800$, $M_w/M_n = 1.31$ (GPC, polystyrene calibration). IR (thin film): ν (cm^{-1}) 1730 (C=O), 1516, 1342 ($-$NO$_2$). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.1$-$1.4 ($-$CH$_3$), 1.9$-$2.3 ($-$CH$_2-$ and $-$CH$_3$), 2.6$-$2.8 ($-$CH$_2$C$-$), 3.4$-$4.0 ($-$NCH$_2-$ and $-$OCH$_2-$), 4.0$-$4.5 ($-$OCH$_2-$), 6.6$-$7.0 (ArH), 7.1$-$7.6 (ArH), 7.6$-$8.0 (ArH), 8.3 (ArH). UV$-$vis (THF, 0.02 mg/mL): λ_{max} (nm) 491.

Preparation of Polymer Thin Films. The polymers were dissolved in tetrahydrofuran (THF; concentration $\sim$ 3 wt %), and the solutions were filtered through syringe filters. Polymer films were spin-coated onto indium$-$tin oxide coated glass substrates, which were cleaned by DMF, acetone, distilled water, and THF sequentially in an ultrasonic bath before use. The 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 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 2); voltage, 7.7 kV at the needlepoint; 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.

Table 2. Maximum Absorption of Polymers (λ_{max}, nm)^a

	P1	P2	P3	P4	P5	P6
THF	488 (492)	492 (497)	492 (498)	491 (497)	470 (484)	472 (490)
CHCl$_3$	483 (486)	490 (493)	489 (492)	490 (493)	455 (460)	461 (468)

^{a} The maximum absorption wavelengths of polymer solutions are given with concentrations fixed at 0.02 mg/mL, while the maximum absorption wavelengths of the corresponding small chromophore molecules in diluted solutions (2.5 × 10^{-5} mol/mL) are given in parentheses.

RESULTS AND DISCUSSION

Synthesis. As demonstrated in Scheme S1 in the Supporting Information, the boronic acids could be easily prepared, following procedures similar to those reported in the literature (15). Under the normal azo coupling reaction conditions, chromophores (**S8** and **S9**) with different functional groups (hydroxyl, aryl bromine, and alkylalkyne) were conveniently obtained. Then "H"-type chromophores could be easily synthesized via a typical Sonogashira coupling reaction between chromophore **S8** (or **S9**) and 1,4-diiodobenzene (**S10**) at room temperature, catalyzed by Pd(PPh$_3$)$_4$, PPh$_3$, and CuI. Generally, Sonogashira coupling reactions were widely used in the field of organic/polymeric light-emitting diodes (16), and here this reaction was handled for the preparation of dendronlike NLO chromophores for the first time, for its mild reaction conditions. When different boronic acid reagents [4-ethoxyphenylboronic acid (BOE), 4-(benzyloxy)phenylboronic acid (BOP), and 4-[4-(naphthalen-1-yloxy)butoxy]phenylboronic acid (BON)] were used, different isolation spacers with different sizes were introduced into the chromophores with moderate yields. Thus, the total route to the synthesis of dendronlike chromophores (**1**$-$**4**) was very simple, making it convenient to compare the tested NLO properties of the resultant polymers with the different sizes of the isolation groups.

The target polyurethanes, **P1**$-$**P4**, were synthesized from the corresponding chromophores and TDI under conditions similar to those reported in the literature for the preparation of polyurethanes (17). Here, the two reactive hydroxyl groups were from the same "H"-type chromophore, and the structures of the resultant polymers were just like those of accordion main-chain polymers, in which the superior alignment could be easily obtained (18). However, the different point was that the linkage position between the two donor$-\pi$-acceptor species in "H"-type chromophores was in the π bridge near the donor side but not tail-to-tail in the accordion
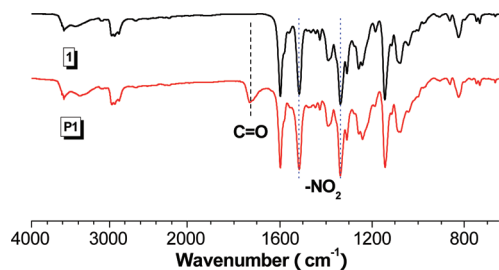
FIGURE 2. IR spectra of polymer P1 and chromophore 1.

polymers. As mentioned previously, different isolation groups were bonded onto the "H"-type chromophore moieties in the π bridge near the donor side, constructing dendronlike structures, which could be termed as dendronlike main-chain polymers. Thus, combined with the advantages of the "H"-type chromophore and the attached "suitable isolation groups", it was expected that this new polymer structure would benefit the orientation alignment during the process of corona poling, and we discuss this point in the NLO Properties section.

Structural Characterization. The newly prepared chromophores and polymers were characterized by spectroscopic methods, and all gave satisfactory spectral data (see the Experimental Section and the Supporting Information for detailed analysis data). The structures of dendronlike chromophores **1−4** were characterized by elemental analysis, and chromophores **2−4** were further confirmed by MALDI-TOF (Figures S1−S3 in the Supporting Information). Figures S4 and S5 in the Supporting Information show the IR spectra of chromophores **S8**, **S9**, **S11**, and **1−4**, in which the absorption bands associated with the nitro groups were at about 1335 and 1515 cm^{-1}. After the chromophores (**1−4**) reacted with TDI, it was easily seen that the absorption bands of the nitro groups remained in the IR spectra of the resultant polymers **P1−P4** (Figures 2 and S6−S8 in the Supporting Information), while another strong absorption peak appeared at about 1730 cm^{-1}, which should be attributed to the vibration of the carbonyl group in a urethane group, indicating polymerization success.

In the ^{1}H NMR spectra of all of the polymers (Figures S9−S12 in the Supporting Information), 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, as shown in the spectrum of **P3** (Figure S11 in the Supporting Information), the signal of the methylene groups linked with the benzene ring in chromophore **3** at about 5.1 ppm, which was a sharp peak, became very broad after the polymerization procedure.

The molecular weights of the polymers were determined by GPC with DMF as an eluent and polystyrene standards as the calibration standards. All of the results are summarized in Table 1, and most of the polymers possessed similar molecular weights, which would perhaps facilitate comparison of their properties on the same level. The polymers were thermolytically resistant, with their TGA thermograms shown in Figure 3, and the 5% weight loss temperatures of the polymers are listed in Table 1. The
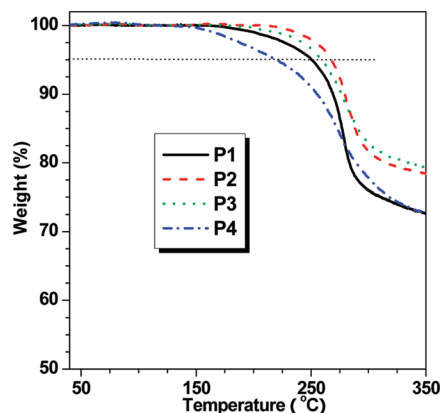

FIGURE 3. TGA thermograms of P1−P4, measured in nitrogen at a heating rate of 10 °C/min.
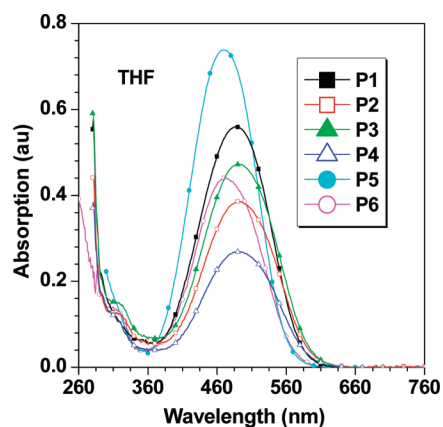

FIGURE 4. UV−vis spectra of THF solutions of polymers P1−P6 (0.02 mg/mL).

results show that all of the polymers exhibited good thermal stability up to around 250 °C. The glass transition temperature (T_g) of the polymers were investigated using a differential scanning calorimeter (Table 1 and Figure S13 in the Supporting Information). The relatively low T_g should be attributed to the introduction of flexible dendrons, which destroyed the rigidity of the polymer backbone, similar to that reported in the literature (19).

UV−Vis Spectra and Site-Isolation Effects. All of the polymers were soluble in common polar organic solvents such as chloroform, THF, DMF, and dimethyl sulfoxide (DMSO). The UV−vis absorption spectra of polymers and chromophores in different solvents are shown in Figures 4, 5, S14 and S15 in the Supporting Information, and the maximum absorption wavelengths for the $\pi-\pi^*$ transition of the azo chromophore moieties in them are listed in the Experimental Section and Table 2. In addition, in order to investigate the advantages of the dendronlike structure, the polymers **P5** and **P6** (Chart 1) were prepared for comparison, in which the push−pull structures of the chromophore moieties were the same but the types of chromophores were linear. For **P5**, no isolation groups were introduced, and for **P6**, only BOE was used as an isolation moiety, the same as **P2**. The UV−vis absorption spectra of **P5** and **P6** are shown in Figures 4 and 5, and their maximum absorption wavelengths are also listed in Table 2.
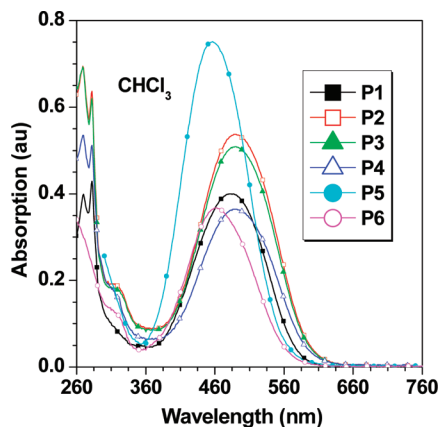
FIGURE 5. UV–vis spectra of CHCl₃ solutions of polymers P1–P6 (0.02 mg/mL).

It was easily seen that, after being bonded to the polymer chain, the maximum absorptions of the chromophore moieties of all of the polymers (P1–P6) were blue-shifted compared with those of the free chromophore molecules, indicating the presence of the electronic interaction between the chromophore moieties and the polymer chain (17). However, compared to those of linear polymers P5 and P6 (up to 18 nm in THF), the blue-shifted extent of the dendronlike main polymers P1–P4 sharply reduced (not larger than 6 nm in THF). This was understandable: as discussed in the Synthesis section, in P1–P4, there was only one reactive group (hydroxyl group) for one piece of donor–π-acceptor structure in their corresponding small chromophore molecules 1–4 (if we considered that there were two pieces of donor–π-acceptor structure in the "H"-type chromophores), while in P5 and P6, there were reactive groups for one donor–π-acceptor structure in the corresponding chromophores, leading to the strengthened electronic interaction between the chromophore moieties and the polymer chain in P5 and P6 after the chromophores were introduced into the polymer backbone, in comparison with those of P1–P4. Thus, the blue-shifted extent of P1–P4 should be reduced, further confirming the presence of the electronic interaction between the chromophore moieties and the polymer chain.

On the other hand, because the "H"-type chromophores in P1–P4 were surrounded by bulky isolation spacers, the aggregation of chromophores could be reduced efficiently. Therefore, we investigated the isolation effect by a comparison of their maximum absorptions in THF and chloroform solutions, according to the literature method (20). From Figures S16–S21 in the Supporting Information and Table 2, it was easily seen that the maximum absorption wavelength of P5 in a THF solution was 470 nm, but 455 nm in chloroform (15 nm blue-shifted), while those of P1–P4 were only blue-shifted 1–5 nm. The reduced solvatochromic shifts should be attributed to the isolation effect, indicating that the introduced isolation groups could shield the chromophores from the solvent effect. The blue-shifted extent of P6 (9 nm) is smaller than that of P5, because of the usage of BOE as isolation groups; however, it was still much larger than that of P2 (2 nm). The phenomena were not strange

because, in comparison with P6, there was another isolation group (dialkyne benzene moieties) present in the π bridge near the acceptor side in P2 that could more efficiently protect the chromophore moieties from attack of the solvent molecules. Therefore, the obtained results demonstrated the advantages of the "dendronlike main-chain" structure of P1–P4, in which the chromophore moieties were well encapsulated. These advantages should surely decrease the strong intermolecular dipole–dipole interactions of the polar chromophore moieties and benefit the NLO effect of the polymers.

The UV–vis investigation of chromophores was consistent with the results of the polymers (Table 2 and Figures S14 and S15 in the Supporting Information). While the solvent was changed from THF to chloroform, the maximum absorptions of the linear chromophores S13 and S14 (Chart S3 in the Supporting Information) were blue-shifted 22–24 nm; however, the maximum absorptions of "H"-type chromophores (1–4) were only blue-shifted less than 6 nm in these two solvents, displaying the superior structure of the "H" shape.

NLO Properties. To evaluate the NLO activity of the polymers, their poled thin films were prepared. The convenient technique to study the second-order NLO activity is to investigate the SHG processes characterized by d_{33}, an SHG coefficient. Calculation of the SHG coefficients (d_{33}) for the poled films is based on the following equation (21):

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

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 factor of the apparatus and is equal to 1.2 when $l_c \gg l_s$. From the experimental data, the d_{33} values of P1–P4 were calculated at a fundamental wavelength of 1064 nm. The poling conditions and measured d_{33} values of these polymers were similar to those used previously (22) and are summarized in Table 1.

Here, the obtained NLO results were encouraging, and all of the polymers demonstrated relatively large d_{33} values, because of the dendronlike structure. P1 exhibited a d_{33} value as high as 118.6 pm/V, which was over 2 times that of the linear polymer P5 (56.6 pm/V) (9a), although their loading densities of effective chromophore were nearly the same (0.573 for P1 and 0.591 for P5). In the "H"-type chromophores, there was a bulky dialkyne benzene moiety present between the two donor–π-acceptor species that acted as isolation spacers and could reduce the intermolecular electrostatic interaction effectively to increase the poling efficiency; thus, the NLO effects should be enhanced. Also, in comparison with other polymers containing "H"-type chromophores, for example, PS2–PS4 in Charts S1 and S2 in the Supporting Information, P1–P4 demonstrate higher

Chart 1
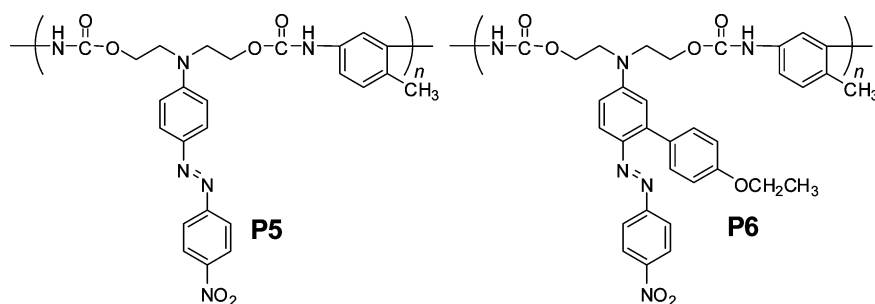
NLO effects, indicating that the dialkyne benzene moieties are better isolation groups than those in **PS2−PS4**.

According to the concept of "suitable isolation groups", for a given chromophore moiety and a given linkage position, there should be a suitable isolation group present to efficiently boost its microscopic β value to possibly a higher macroscopic NLO property; we introduced different isolation groups from small size (BOE) to larger ones (BON) into the "H"-type chromophore to further adjust its structure. As expected, the d_{33} values were not always increasing as the isolation groups enlarged. Figure 6A shows a comparison of the d_{33} values of the polymers, using **P1** as a reference. Considering the effects of different molar concentrations of the active chromophore moieties in the polymers, we used the tested d_{33} values by dividing the molar concentrations of the active chromophores and compared the results again with that of **P1** as the reference (Figure 6B). It was easily seen that the trends of the two curves are the same, and in this system, the BOE group was a good isolation group, proving our previous idea. As there might be some resonant enhancement due to the absorption of the chromophore moieties at 532 nm, the NLO properties of **P1−P4** should be smaller, as shown in Table 1 ($d_{33}(\infty)$), which were calculated by using the approximate two-level model. Also, we drew the curve, still using that of **P1** as a reference (Figure 6C), and the trend was similar to the previous ones.
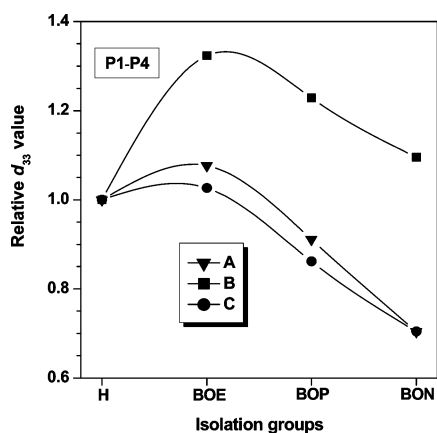
It was noted that the d_{33} value of **P2** was only enhanced up to about 10 pm/V in comparison with that of **P1**, unlike our previously reported polymers (12, 13), in which the d_{33} values could increase almost 2 times through the introduction of the suitable isolation groups. In addition, the size of BOE was much smaller than that of carbazole groups, which were suitable groups for the chromophores with nitro as acceptors in our previous work (9a). This point demonstrated the advantages of the "H"-type structure again on another side, and here, in the "H"-type chromophore, the dialkyne benzene might already be a suitable isolation group for the present donor−π−acceptor structure and could well balance the two important influencing factors for the resultant d_{33} values of the polymers (the loading density of chromophores and the poling efficiency) simultaneously. Therefore, further modifying the subtle "H" structure could not improve the poling efficiency of the resultant polymers to a large degree, and the reduced loading density of the chromophore moieties might lead to the decreased d_{33} values, such as **P3** and **P4**. These experimental results, from another point of view, indicated that the usage of "H"-type chromophores might be an alternative approach to solving the present challenge in the field of NLO research as mentioned above: how to efficiently translate the large β values of the organic chromophores into high macroscopic NLO activities of polymers.

To further study the alignment behavior of the chromophore moieties in the polymers, the order parameter (Φ) of the polymers (Table 1) was also measured and calculated from the change of the UV−vis spectra of their thin films before and after corona poling under an electric field,
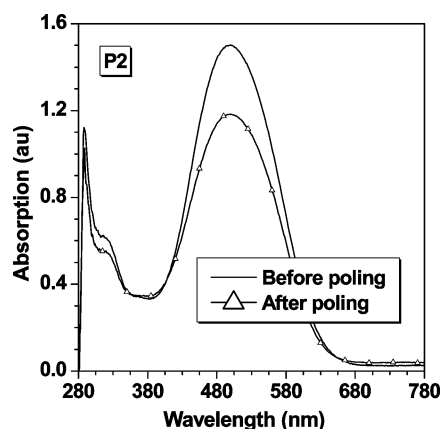

FIGURE 6. (A) Comparison of the d_{33} values of the polymers. (B) Comparison of the calculated d_{33} values, which were obtained by using the tested d_{33} values of the polymers by dividing the concentrations of the active chromophore moieties of the polymers. (C) Comparison of the calculated d_{33} (∞) values of the polymers, according to the approximate two-level model, using P1 as the reference.

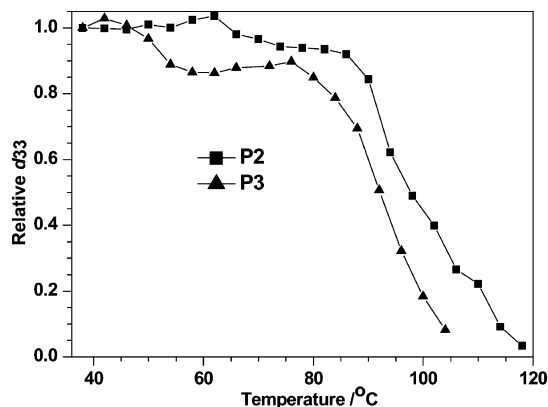FIGURE 7. Absorption spectra of the film of P2 before and after poling.

FIGURE 8. Decay curves of the SHG coefficients of P2 and P3 as a function of the temperature.

according to the equation described in Table 1 (footnote i). Figure 7 showed the UV−vis spectrum of the film of **P2** before and after corona poling as an example. The spectra of other polymers are demonstrated in Figures S22−S24 in the Supporting Information. The tested Φ values were well in accordance with their d_{33} values, and BOE was also confirmed as the suitable group. **P1** exhibited a higher Φ value (0.20) than those of the reported linear polymers, which fully displayed the good alignment of the "H"-type chromophore moieties in polymers. After BOE was introduced as isolation groups, the Φ value of **P2** was further increased 1.3 times (0.26), indicating our original idea: the poling efficiency may be adjusted by controlling the shape of the "H"-type chromophores. However, because of the reduced loading density of chromophores, the d_{33} value of **P2** was only enhanced about 10 pm/V.

The dynamic thermal stabilities of the NLO activities of **P2** and **P3** 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 120 °C in air at a rate of 4 °C/min. As shown in Figure 8, the long-term temporal stability of **P2** was relatively good, and the onset temperature for decay in the d_{33} value was around 90 °C, making it a good candidate for practical applications.

CONCLUSION

A series of dendronlike NLO polyurethanes embedded with "H"-type chromophores were successfully designed and synthesized for the first time. By application of the concept of "suitable isolation groups", different sizes of isolation groups were introduced into "H"-type chromophores to optimize their structure. The obtained NLO results demonstrated that all of the polymers exhibited large NLO effects because of their unique structure and the enhancement of the d_{33} values and poling efficiency of **P2** indicated that the "H"-type chromophore moieties also needed to be adjusted to achieve better performance. Thus, it is suggested that the utilization of "H"-type chromophores might be a promising choice to efficiently translate the large β values of the organic chromophores into high macroscopic NLO activities of polymers.

Supporting Information Available: Charts of the structures of some chromophores and polymers, detailed synthetic procedures and characterization data for the monomers, and figures of FTIR spectra, MALDI-TOF spectra, ^{1}H NMR spectra, UV−vis spectra, DSC curves, and absorption spectra of polymers before and after poling. This material is available free of charge via the Internet at http://pubs.acs.org.

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