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An Attempt To Modify Nonlinear Optical Effects of Polyurethanes by Adjusting the Structure of the Chromophore Moieties at the Molecular Level Using "Click" Chemistry

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Introduction

Because of their potential application in high-speed electro-optic (EO) devices with very broad bandwidth and low driving voltages, organic second-order nonlinear optical (NLO) materials have attracted much attention among scientists.[1,2] One of the major problems encountered in optimizing organic NLO materials is to efficiently translate the large β values of the organic chromophores into high macroscopic NLO activities of polymers. To solve this problem, it is badly needed, in some degree, to overcome or minimize the strong intermolecular dipole−dipole interactions of NLO chromophores during their poling-induced noncentrosymmetric alignment. Just this interaction accounts for the fact that the NLO properties of the polymers are only enhanced several times even if the $\mu\beta$ values of chromophores have been improved by up to 250-fold, thanks to the great efforts of scientists in the past decades.[3]

Fortunately, it is proved to be an efficient approach for minimizing this interaction and enhancing the poling efficiency to control the shape of the chromophore, with spherical shape, proposed by Dalton et al.,[4] being the most ideal conformation. Applying the site isolation principle,[5] many dendrimers and polymers containing dendronized chromophores have been demonstrated to exhibit large EO coefficients, in which some bulky groups were linked to chromophores as the isolation moieties.[6] These isolation parts in the chromophore moieties could surely weaken the strong intermolecular electrostatic interaction to enhance the resultant macroscopic NLO effect of polymers, but on the other hand, meanwhile, they would dilute the active concentration of the chromophore moieties, usually leading to the reduced EO coefficients. Thus, there should be a balance present to tune up these two effects. However, there are no reports concerned on this question, and we still do not know how to choose favorite isolation groups to boost the fixed microscopic β value of a NLO chromophore to possible higher macroscopic NLO property of polymers containing this chromophore efficiently. Also, the synthetic methods for the linkage of the isolation groups to chromophores are a little difficult; for example, the reaction time is relatively longer and the purification is not so simple in the frequently used ester reactions.

To deepen the exploration of the fundamental architectural design parameters, based partly on our previous research,[7] in this work we tried to modify the NLO properties of the resultant polymers by adjusting the structure of the chromophore moieties at the molecular level by introducing different size of isolation spacers (Scheme 1). Also, to facilitate the preparation procedure, 1,3-dipolar azide−alkyne reactions, "click" chemistry,[8] has been used to link the isolation spacers to the chromophores. To the best of our knowledge, it is the first time that this type of "click" reaction was used in the NLO field.

Results and Discussion

As shown in Scheme 1, **P2−5** were prepared by the copolymerization of 2,4-toluene diisocyanate (**1**) and the corresponding chromophores (**2−5**) under similar conditions as reported in the literature.[9] For comparison, **P1**, nearly without isolation groups, was also synthesized. The experimental details, including the polymerization process of **P1−5** and the preparation procedure for chromophores **2−5**, are described in the Supporting Information. It should be pointed out that chromophores **2−5** could be easily obtained through the "click" chemistry reaction due to its high efficiency and technical simplicity.[8] The reaction products were characterized by spectroscopic analyses, and all the polymers (**P1−5**) gave satisfactory data (some data listed in Table 1) corresponding to their expected molecular structures (see Supporting Information for details). The ^{1}H NMR spectra of **P4** and its corresponding chromophore **4** are given in Figure 1 as an example. The chemical shifts of **P4** show an inclination of signal broadening with comparison to those of chromophore **4** due to polymerization. And there are some small peaks present downfield besides those signals derived from the chromophore moieties, which are assigned to the urethane units formed in the polymerization process,[9] confirming the successful reaction between chromophore **4** and comonomer **1**. The strong absorption peak at about 1720 cm^{-1} in the IR spectra of polymers (Figure S1) was attributed to the vibration of the carbonyl group in urethane groups, further proving the formation of urethane linkages during the polymerization process.

All the polymers are soluble in common polar organic solvents, such as THF, DMF, and DMSO. The UV−vis absorption spectra are shown in Figure S2, and the maximum absorption wavelength for the $\pi-\pi^*$ transition of the azo moieties in them are listed in the Experimental Section and Table 1. After being bonded to the polymer chain, the maximum absorption wavelength of the chromophore moieties were blue-shifted (up to 18 nm in the case of **P3**), compared with those of the free chromophore molecules, indicating the presence of the electronic interaction between the chromophore moieties and the polymer chain.[9] All the polymers exhibit nearly the same maximum absorption wavelengths, indicating that the presence of the different isolation spacers does not influence the electronic properties of the chormophore moieties, which would ensure the comparison of their NLO properties at the same level. The polymers are thermally stable (Figure S3), and the 5% weight loss temperatures of polymers are listed in Table 1. **P2−5** exhibit much better thermal stability than **P1**, showing that the introduction of the isolation groups to the chromophore would benefit the stability against heating. The glass transition temperature (T_g) of the polymers becomes higher with the increasing of the size of the isolation spacers (Table 1).

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Scheme 1

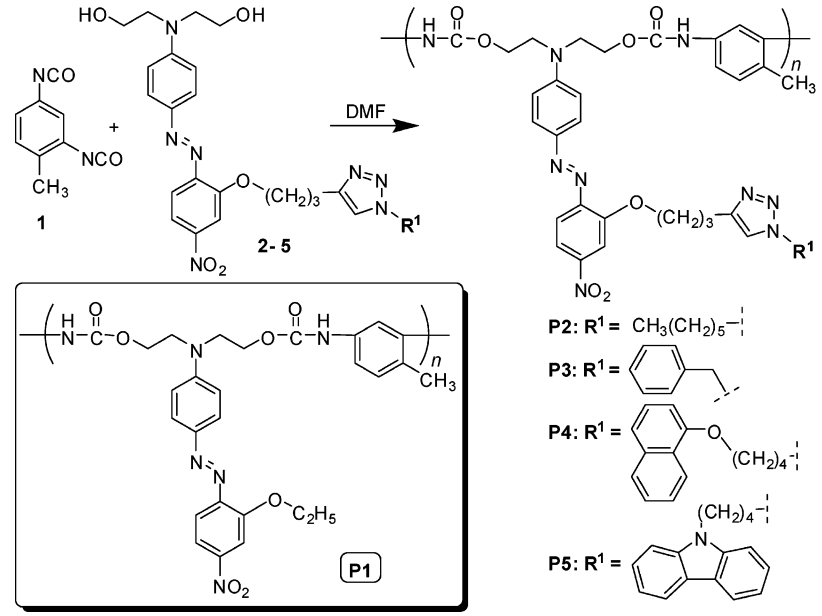

Table 1. Polymerization Results and Characterization Data

no.	yield (%)	M_w[a]	M_w/M_n[a]	λ_{max}[b] (nm)	T_g[c] (°C)	T_d[d] (°C)	T[e] (°C)	l_s[f] (μm)	d_{33}[g] (pm/V)	Φ[h]
P1	60.7	1.94	1.08	472 (488)	86	185	105	0.20	54.4	0.08
P2	73.3	3.72	1.28	472 (487)	87	272	90	0.21	68.8	0.14
P3	81.5	3.09	1.18	470 (488)	107	272	120	0.20	74.8	0.22
P4	76.6	2.93	1.20	472 (488)	100	257	109	0.25	56.3	0.20
P5	81.8	2.59	1.17	472 (487)	113	268	125	0.32	45.4	0.17

[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 wavelengths of the corresponding small chromophore molecules in diluted THF solutions are given in 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 nitrogen at a heating rate of 20 °C/min. [e] The best poling temperature. [f] Film thickness. [g] Second harmonic generation (SHG) coefficient. [h] 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.

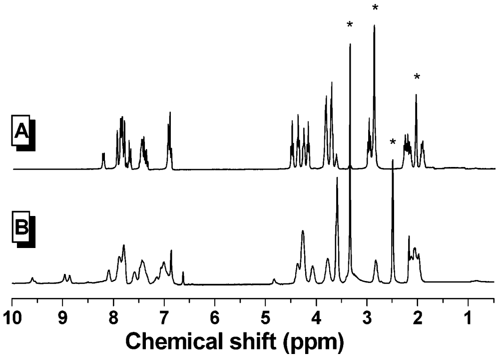

Figure 1. ^{1}H NMR spectra of chromophore **4** (A) in acetone-d_6 and **P4** (B) in DMSO-d_6. The solvent peaks are marked with asterisks (*).

To evaluate the NLO activity of the polymers, the poled thin films of polymers are 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. The method for the calculation of the SHG coefficients (d_{33}) has been reported previously.[7] From the experimental data, the d_{33} values of **P1**−**5** are calculated at the 1064 nm fundamental wavelength (Table 1). It is not strange that the polymers demonstrate different d_{33} values for their different structure. However, the d_{33} values do not always increase with increasing size of the isolation spacer. **P3** shows the highest data, and when the isolation groups are more bulky than benzyl moieties, the NLO effects decrease. The phenomena seem strange but understandable. The linkage of the isolation group would mainly cause three impacts: (1) to minimize the strong intermolecular dipole−dipole interactions to some degree, leading to the improvement of the d_{33} values of the polymers; (2) to dilute the active concentration of the chromophore moieties, generally reducing the d_{33} values; and (3) to increase the bulky 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, the macroscale NLO properties of polymers containing dendronized chromophores as side groups are expected to be heavily related to the subtle difference in architectural design. And in our case, for this kind of chromophore, the suitable isolation group should be as shown in **P3**. The obtained preliminary results demonstrate that for a given chromophore moiety and a given linking position there should be a suitable isolation group present to boost its microscopic β value to possible higher macroscopic NLO property efficiently. From this point, even higher NLO properties could be obtained by using the present chromophores if we choose more suitable isolation spacers. However, to further study the structure−property relationship of NLO polymers in detail, to realize the widely practical application of NLO materials, much work is still needed.

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 films before and after

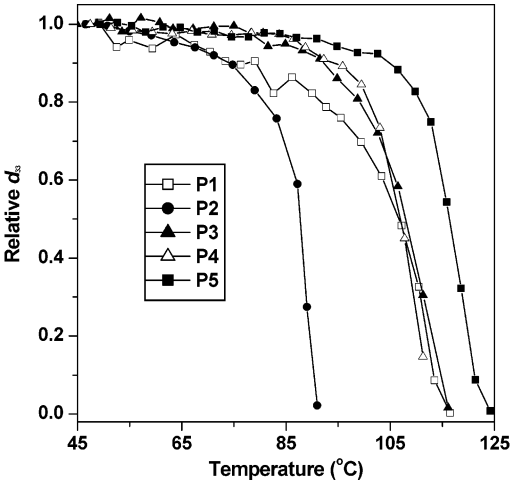

Figure 2. Decay of SHG coefficient of polymers as a function of temperature.

corona poling under electric field (Figure S4−8), according to the equation described in Table 1 (footnote *h*). While the isolation groups enlarged, the Φ values increase, reach a peak point (tested in **P3**), and then decrease even the isolation spacers become more bulky. These results confirm the above discussion and further prove that there is really a balance present when different isolation spacers are bonded to the chromophore moieties. Thus, to boost the microscopic β value of a chromophore to possibly higher macroscopic NLO property of polymers containing this chromophore efficiently, it is important to choose a suitable isolation spacer to meet the optimized point in the balance caused by the introduction of the isolation spacers.

The dynamic thermal stabilities of the NLO activities of the polymers (Figure 2) are investigated by depoling experiments, in which the real time decays of their SHG signals are monitored as the poled films are heated from 40 to 150 °C in air at a rate of 4 °C/min. The results showed that the introduction of the large size of the isolated groups to the chromophores benefits the thermal stability of the resultant polymers, and **P5** exhibits the best thermal stability with the onset temperature for decay at about 110 °C.

Conclusion

In summary, an attempt is reported to modify nonlinear optical effects of polyurethanes by adjusting the structure of the chromophore moieties at the molecular level conveniently by using the "click chemistry" reaction. Our preliminary results proved that the NLO properties of the polymers do not always increase accompanying with the enlargement of the isolation groups linked to the corresponding chromophore moieties, and there is a suitable isolation group present for a chromophore to boost its microscopic β value to possibly higher macroscopic NLO property in polymers efficiently. Further study is still under way in our lab.

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Supporting Information Available: Detailed synthetic procedures and characterization data for the monomers and polymers; figures of FT-IR spectra, ^{1}H NMR spectra, UV−vis spectra, TG 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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