Convenient Attachment of Highly Polar Azo Chromophore Moieties to Disubstituted Polyacetylene through Polymer Reactions by Using "Click" Chemistry

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Received April 11, 2007
Revised Manuscript Received June 25, 2007

Polyacetylene (PA) has attracted increasing interest in recent years as the best known conjugated polymer. Thanks to the enthusiastic efforts of polymer scientists, thousands of mono- or disubstituted PAs have been prepared, and the research fields were extended from the initial traditional conductive polyacetylene to the modern liquid crystals, polymeric light emitting diodes, helical polymers, gas separation membranes, organic−inorganic hybrids, nonlinear optical and magnetic materials, etc.[1−3] We have been interested in designing new functional PAs by modifying the substituents attached to the acetylene monomers at the molecular level, and successfully obtained hundreds of monosubstituted and lots of disubstituted PAs. In contrast to the monosubstituted acetylenes, it is nearly impossible, or in other words, a big challenge, for many disubstituted acetylenes with active protons or polar moieties to be polymerized to yield their corresponding polyacetylenes, though disubstituted PAs are generally superior to their monosubstituted counterparts in performance.[3] To solve this problem, we recently attempted to obtain functional disubstituted PAs inaccessible by the polymerization of their monomers, from PA intermediates containing reactive groups on the side chains, through polymer reactions. The results were exciting, and some new functional disubstituted PAs were successfully obtained, including the first example of second order nonlinear optical (NLO) active polyacetylene, which demonstrates the beneficial effect of the rigid conjugated PA backbone in NLO materials.[4] This prompted us to further prepare a new series of NLO active PAs, which could not be obtained from their corresponding monomers, and systematically study their properties, based partially on our recent work on NLO polymers,[5] since NLO materials possess huge potential applications in high-speed electro-optic (EO) devices.[6] As there are some limitations present in the previous reactive PA intermediates, new synthetic strategies still need to be explored.

On the other hand, the 1,3-dipolar cycloadditions of azides with alkynes catalyzed by copper(I) complexes under mild conditions, known as "click reaction", has been recently receiving much attention as a highly efficient and stereoselective reaction coupled with excellent functional group compatibility.[7] The click-chemistry strategy has been successfully applied to macromolecular chemistry, affording polymeric materials varying from block copolymers, dendrimers, to complex macromolecular structures.[8] Many functional groups could be attached to different polymeric backbones to construct new functional polymers conveniently through "click reaction"; however, so far, there are no reports concerned on the introduction of polar organic moieties to PA system by using this click-chemistry strategy. In this report, we present such examples. We applied the concept of "click chemistry" to attach highly polar azo moieties to disubstituted PAs for NLO applications for the first time.

As demonstrated in Scheme 1, PAs **P1**−**P10** were prepared by the click reaction between azido-containing poly(1-phenyl-1-pentyne) **P0**, which was synthesized according to our previously reported procedure,[9] and the predesigned NLO chromophores (**1**−**10**). It should be pointed out that in these ten polymers, the modes of the linkage of chromophore moieties to the PA backbone are not the same, and we will discuss this later. The experimental details, including the post functional process for **P1-10** and the preparation procedure for chromophores (**1**−**10**), are described in the Supporting Information. The reaction progress was monitored by FT-IR spectroscopy as the azido groups absorb strongly centered at about 2096 cm^{-1}, and all the reactions proceeded completely quickly in about 2 h, indicated by the disappearance of the peak at 2096 cm^{-1} in the FT-IR spectra.

The reaction products were characterized by spectroscopic analyses, and all the polymers (**P1**−**P10**) gave satisfactory data (some being listed in Table 1) corresponding to their expected molecular structures (see Supporting Information for details). As shown in their IR spectra (Figure S1−S3), not only the absorption peak of the azido groups, but also the $\equiv$C−H stretching vibrations of chromophores at about 3298 cm^{-1}, disappeared in **P1**−**P10**, while new absorption bands associated with the nitro or sulfonyl groups appeared at about 1335 or 1129 cm^{-1}, indicating the successful attachment of the NLO chromophore moieties to PA backbone. This was further proved by their ^{1}H NMR spectra (Figure S4 as a typical example).

All the polymers are soluble in common polar organic solvents, such as THF, DMF, and DMSO. The UV−vis absorption spectra are shown in Figures S5 and S6, and the maximum absorption wavelengths 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 wavelengths of the chromophore moieties were nearly the same as those of the free chromophore molecules, similar to our previous case.[4b] The polymers are thermally stable (Figure S7), and the 5% weight loss temperatures and the glass transition temperature (T_g) of polymers are listed in Table 1.

The NLO activity of the polymers were measured similar as we reported previously,[5,10] and from the experimental data, the d_{33} values of **P1**−**P10** are calculated at the 1064 nm fundamental wavelength (Table 1). From their structure (Scheme 1), it is easily seen that polymers could be divided into three different kinds except **P4**: **P1**−**P3**, **P5**−**P7**, and **P8**−**P10**, which could be considered as corresponding to the cartoon models of **I**, **V**, and **IV** demonstrated in Chart 1. For each kind of polymers, the linked isolation group (labeled as R^2 or R^3 or R^4 in Scheme

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10.1021/ma070846o CCC: \$37.00

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)	$d_{33(\infty)}$[h] (pm/V)	Φ[i]
P1	52.0	19 000	1.61	485 (485)	119	275	128.1	0.43	72.4	9.7	0.14
P2	92.6	24 900	1.71	488 (490)	129	301	141.1	0.22	130.5	19.3	0.19
P3	92.9	26 000	1.88	495 (490)	107	293	108.7	0.35	52.9	5.6	0.15
P4	74.3	18 000	1.48	451 (448)	126	288	137.8	0.94	21.2	4.9	0.18
P5	75.7	21 400	1.70	490 (491)	105	273	111.0	0.42	62.8	7.5	0.12
P6	97.3	25 400	1.60	465 (467)	86	290	67.7	0.51	34.1	6.5	0.10
P7	98.6	21 000	1.55	465 (467)	84	210	88.7	0.45	25.1	4.8	0.09
P8	93.4	21 000	1.55	448 (453)	116	271	122.5	0.33	48.7	11.7	0.16
P9	78.4	23 400	1.51	430 (433)	95	298	87.0	0.38	53.2	15.4	0.17
P10	99.1	24 000	1.52	431 (434)	93	278	101.8	0.43	28.8	8.3	0.08

[a] Determined by GPC in THF 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 are 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.

Scheme 1

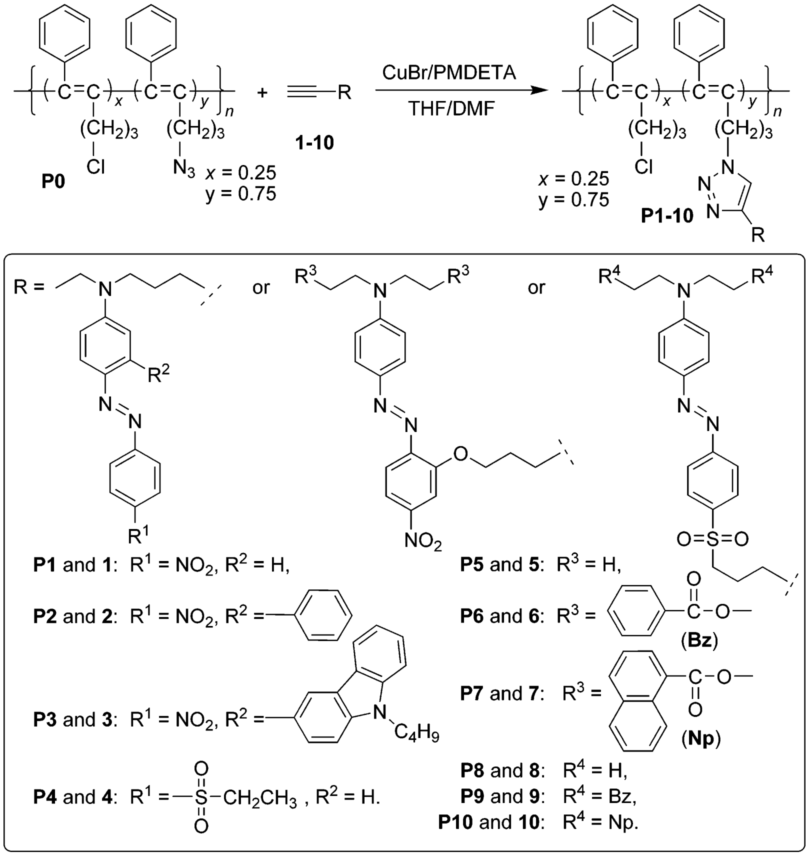
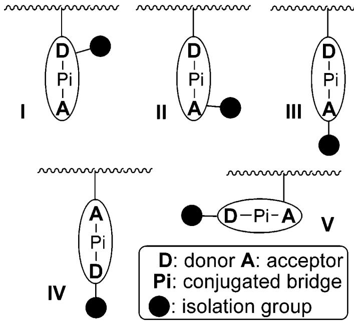


Chart 1



1) to the chromophore moieties, changed from small size group (hydrogen atom) to larger ones (carbazolyl or naphthalene moieties).

According to the site isolation principle,[11] the introduced isolation groups would weaken the strong intermolecular electrostatic interaction (which 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),[12] to enhance the resultant macroscopic NLO effect of polymers. Just in 2006, we prepared several series of NLO polymers, and they should belong to the cartoon models of **I**, **II**, and **III** (Chart 1). On the basis of the obtained experimental data so far, we proposed that there is a suitable isolation group present for a special chromophore at a fixed linkage position, to boost its microscopic β value to possibly higher macroscopic NLO property in polymers efficiently.[5] As the supporting proofs are still weak, and the previous results were built on different comparing levels, such as different molecular weights, thus, we would like to test our ideas with

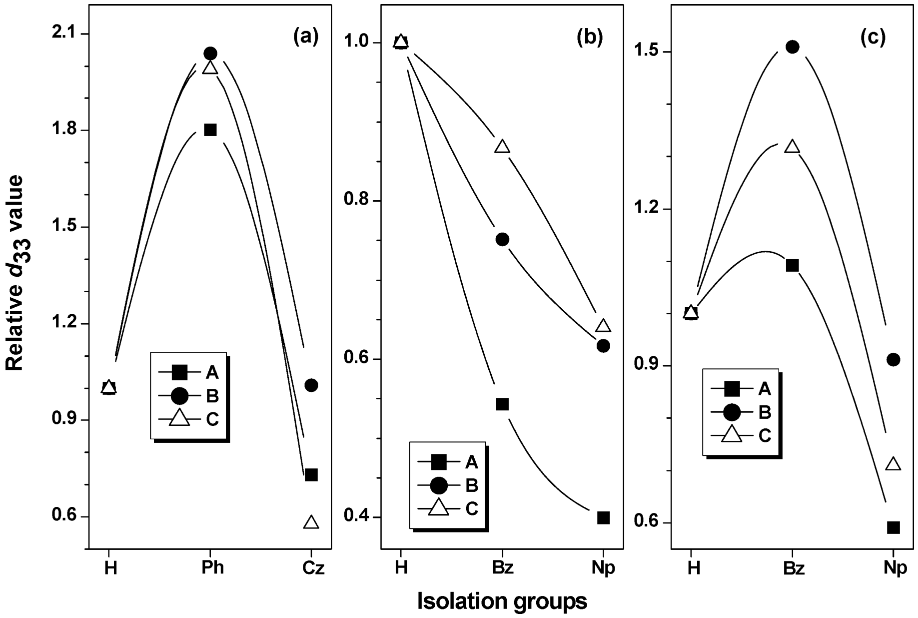


Figure 1. Analysis of the obtained NLO data of polymers (a) **P1−P3**, (b) **P5−P7**, and (c) **P8−P10**. Key: (A) comparison of the d_{33} values of the polymers; (B) comparison of the calculated d_{33} values, which were obtained by using the tested d_{33} values dividing the concentration of the active chromophore moieties of the polymers; (C) comparison of the calculated $d_{33(\infty)}$ values according to the approximate two-level model, using **P1** for **P1−P3**, **P5** for **P5−P7**, and **P8** for **P8−P10** as a reference.

different linkage models of the isolation groups on the chromophore moieties, while on the possibly same molecular level. Therefore, here, in this paper, we designed the above-reported three types of NLO PAs (the cartoon models of **I**, **V**, and **IV**). From the previous cases, model **I** was selected to have a further check, and two new models, **V** and **IV**, were freshly added. As all 10 PAs were derived from the same starting reactive polyacetylene **P0**, their NLO properties could be compared nearly on the same level. Actually, the structural characterization data partially proved this point, for example, the similar molecular weights and thermal behavior. This is another advantage of our PA system, which should be attributed to the powerful ability of click chemistry.

To study the NLO results more visually, we compared the d_{33} values of the polymers using that of **P1** for **P1−P3**, **P5** for **P5−P7**, and **P8** for **P8−P10** as reference (the three labeled A curves in Figure 1). When the isolation groups changed from hydrogen atom to the phenyl group, the d_{33} value of **P2** increased to 1.8 times that of **P1**; however, the tested NLO effect decreased dramatically while the size of the isolation moieties (carbazolyl groups here in **P3**) further increased (curve A in Figure 1a). Similar phenomena were found in the system of **P8−P10**: the d_{33} values will increase and achieve to a maximum peak while the size of the isolation groups enlarging, then decrease quickly as the isolation moieties become even larger. This trend is the same as we observed before, further proving our hypothesis about the effect of the isolation groups linked in the chromophore moieties.[5] On the contrary, **P5** demonstrates the highest d_{33} value in the system of **P5−P7**, and after some isolation moieties bonded to the chromophore groups at the donor side, the NLO effects of the resultant polymers, **P6** and **P7**, decrease quickly, though the isolation groups in them are the same as those in **P8** and **P9**, respectively. Since the introduction of different isolation groups would lead to different molar weights of the obtained chromophore moieites, resulting in diluted concentration of the active chromophore moieties in the polymers, we compared the NLO results again, using the tested d_{33} values, dividing the concentration of the active chromophore moieties in PAs, according to the one-dimensional rigid orientation gas model (eq S1). As shown in Figure 1 (the three labeled B curves), the results are similar to those indicated by the three labeled A curves. Considering there might be some resonant enhancement due to the absorption of the chromophore moieties at 532 nm, we calculated the $d_{33(\infty)}$ values of PAs by using the approximate two-level model (Table 1).

Again, the trends (the three labeled C curves in Figure 1) are similar as the two ones discussed above. The changing trends corresponding to the increasing of the size of the isolation groups, further confirmed by the order parameter (Φ) of the polymers (Table 1 and Figure S8), which were measured and calculated from the change of the UV−vis spectra of their films before and after corona poling under electric field (Figures S9−18), according to the equation described in Table 1 (footnote *i*).

Therefore, for the first time, our results obtained in the system of **P5−P7** indicate that the introduction of the isolation groups to the chromophore moieties not always benefit the NLO properties of the resultant materials, or we could say, the hydrogen atoms are the best isolation moieties in some special cases. Thus, the NLO properties of **P1−P10** further confirmed our previous idea about the effect of the bonded isolation groups.

In conclusion, the "click" chemistry was, for the first time, applied to realize the attachment of highly polar azo chromophores to disubstituted PA conveniently. Our preliminary results demonstrate: (1) **the introduction of the isolation groups to the chromophore moieties does not always improve the NLO effect of the resultant materials**; (2) the linkage model between the polymer backbone and the side chain affects the NLO properties of the resultant polymer in some degree; (3) 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; (4) the good NLO properties of **P1−P10**, coupled with their good thermal stability, make them good candidates for practical photonic applications. Further study is still underway in our lab.

Acknowledgment. Z.L. is grateful to the National Science Foundation of China (no. 20674059, 20402011), the National

Fundamental Key Research Program and Hubei Province for financial support. B.Z.T. thanks the Research Grants Council of Hong Kong (Project Nos. 602706, 603505 and HKU2/05C).

Supporting Information Available: Text giving detailed synthetic procedures and characterization data for the monomers, scheme showing the reactions, and figures of FT-IR spectra, ^{1}H NMR spectra, UV−vis spectra, TGA curves, order parameter (Φ) of polymers, and absorption spectra of polymer thin films before and after poling. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA070846O