Macromolecules **2009**, *42*, 1589−1596

New Azo-Chromophore-Containing Hyperbranched Polytriazoles Derived from AB_2 Monomers via Click Chemistry under Copper(I) Catalysis

Zhong'an Li,[†] Gui Yu,[‡] Pan Hu,[†] Cheng Ye,[‡] Yunqi Liu,[‡] Jingui Qin,[†] and Zhen Li*,[†]

Department of Chemistry, Hubei Key Laboratory on Organic and Polymeric Opto-Electronic Materials, Wuhan University, Wuhan 430072, China, and Organic Solids Laboratories, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, China

Received November 11, 2008; Revised Manuscript Received January 9, 2009

ABSTRACT: By modifying the synthetic procedure, the previous reported impossible approach was successfully utilized to construct new azo-chromophore-containing hyperbranched polymers (**HP1** and **HP2**) from AB_2 monomers through click chemistry reactions with the aid of copper(I) catalysis. The two polymers were soluble in organic solvents and well characterized. Thanks to the advantages of the hyperbranched polymeric structure, the two polymers demonstrated good NLO properties, making them promising candidates for the practical applications.

Introduction

In recent years, the "click" chemistry has aroused much interest among researchers because of its remarkable features such as nearly quantitative yields, mild reaction conditions, broad tolerance toward functional groups, low susceptibility to side reactions, and simple product isolation. Especially, the copper-catalyzed Huisgen cycloaddition, also termed as the Sharpless "click" reaction, is the typical example and has been successfully applied to macromolecular chemistry, affording polymeric materials varying from block copolymers, dendrimers, to complex macromolecular structures.[1−4] However, as to the hyperbranched polymers, the reported examples are still scarce, and most of them took an $A_2 + B_3$ approach,[5a] in which two monomers containing terminal azido and yne groups were needed to construct the hyperbranched polymers through the click chemistry reaction. And it was reported that the Cu(I)-catalyzed click polymerizations of the AB_2 monomers failed to yield soluble polymers due to the self-oligomerization.[5b]

On the other hand, on the basis of the work reported in the literature,[6−11] 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:[12] to efficiently translate the large β values of the organic chromophores into high macroscopic NLO activities of polymers, according to the site isolation principle.[13] Also, our obtained results demonstrated that the introduction of the NLO chromophore moieties to the system of hyperbranched polymers would lead to novel NLO polymers with very large macroscopic NLO effects, partially due to the advantages of hyperbranched polymers, such as the globular structure, the three-dimentional spatial separation of the chromophore moieties.[14] And in comparison with dendrimers, it was much convenient to prepare NLO hyperbranched polymer with one-pot synthesis. But the synthetic methods we used before were based on the normal $A_2 + B_3$ approach. To construct hyperbranched polymers with the structure more like dendrimers to achieve higher macroscopic NLO effects, we would like to prepare new NLO hyperbranched polymers from AB_2 monomers. Considering the remarkable features of the click chemistry reactions mentioned above, it should be ideal to prepare these new polymers via click chemistry.

Thus, partially based on our previous work on the syntheses of linear polymers with the usage of click chemistry reactions,[12b,c,f] we successfully obtained new azo-chromophore-containing hyperbranched polymers **HP1** and **HP2** from AB_2 monomers (Scheme 1) by modifying the synthetic procedure, confirming that the self-oligomerization of AB_2 monomers could be avoided. The two polymers were easily soluble in common organic solvent and well characterized. The tested NLO properties demonstrated that the NLO values were up to 124.4 pm/V; thus, coupled with their convenient synthesis and high thermal stability of the NLO activities, **HP1** and **HP2** could be good candidates for the practical photonic applications. Herein we would like to present the synthesis and characterization of these new hyperbranched polymers in detail.

Experimental Section

Materials and Instrumentation. Chromophores **4** and **5** were prepared as reported previously.[12f] All the other reagents were used as received. ^{1}H NMR and ^{13}C NMR spectra were measured on a Varian Mercury300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer spectrometer-2 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 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 cm^3/min for thermogravimetric analysis (TGA). The thermal transitions of the polymers were investigated using a METTLER differential scanning calorimeter DSC822e 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 Synthesis of Chromophores M1 and M2. Diazonium salt **1** or **3** (1.00 equiv) and compound **2** (1.00 equiv) were dissolved in DMF at 0 °C. The reaction mixture was stirred for 12 h at 0 °C, then treated with H_2O and extracted with CH_2Cl_2 (DCM), and washed with brine. The organic layer was dried

---

* Corresponding author: Ph 86-27-62254108; Fax 86-27-68756757; e-mail lizhen@whu.edu.cn.

[†] Wuhan University.

[‡] The Chinese Academy of Sciences.

10.1021/ma8025223 CCC: $40.75

Scheme 1

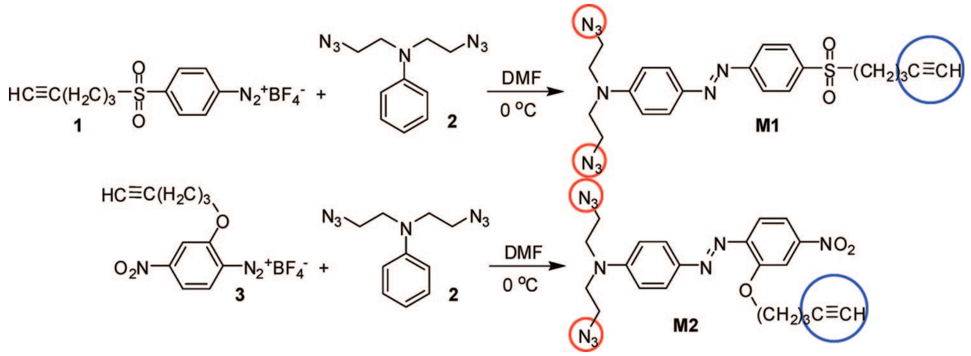


Table 1. Polymerization Results and Characterization Data

polymer	yield (%)	$M_w{}^a \times 10^5$	$M_w/M_n{}^a$	$T_g{}^b$ (°C)	$T_d{}^c$ (°C)	$T_e{}^d$ (°C)	$l_s{}^e$ (μm)	$d_{33}{}^f$ (pm/V)	$d_{33(\infty)}{}^g$(pm/V)	Φ^h
HP1	84.2	4.22	1.22	132	307	160	0.64	77.9	21.7	0.25
HP2	80.8	2.59	1.57	117	254	130	0.48	124.4	22.7	0.22

[a] Determined by GPC in DMF on the basis of a polystyrene calibration. [b] The glass transition temperature (T_g) of polymers detected by the DSC analyses under argon at a heating rate of 10 °C/min. [c] The 5% weight loss temperature of polymers detected by the TGA analyses under nitrogen at a heating rate of 10 °C/min. [d] The best poling temperature. [e] Film thickness. [f] Second harmonic generation (SHG) coefficient. [g] The nonresonant d_{33} values calculated by using the approximate two-level model. [h] Order parameter $\Phi = 1 - A_1/A_0$; A_1 and A_0 are the absorbance of the polymer film after and before corona poling, respectively.

over Na_2SO_4. After removal the organic solvent, the crude product was purified by column chromatography on silica gel using DCM/ethyl acetate (10/1) as eluent.

Chromophore **M1**. Diazonium salt **1** (135 mg, 0.41 mmol), compound **2** (95 mg, 0.41 mmol). The product **M1** was obtained as a red solid (170 mg, 89.0%). IR (thin film), υ (cm^{-1}): 2101 ($-N_3$ and $-C{\equiv}C-$), 1295, 1130 ($-SO_2$). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.98 (m, 3H, $-CH_2-$ and $-C{\equiv}CH$), 2.33 (m, 2H, $-CH_2-$), 3.27 (t, J = 8.1 Hz, 2H, $-SO_2CH_2-$), 3.57 (t, J = 6.0 Hz, 4H, $-N-CH_2-$), 3.71 (t, J = 6.0 Hz, 4H, N_3-CH_2-), 6.80 (d, J = 9.6 Hz, 2H, ArH), 7.96 (d, 2H, J = 8.7 Hz, ArH), 8.00 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$) δ (ppm): 17.5, 22.0, 49.0, 51.0, 55.3, 70.4, 82.0, 112.2, 123.1, 126.5, 129.3, 139.1, 144.7, 150.2, 156.2.

Chromophore **M2**. Diazonium salt **3** (167 mg, 0.52 mmol) and compound **2** (121 mg, 0.52 mmol). The product **M2** was obtained as a deep red solid (202 mg, 84.0%). IR (thin film), υ (cm^{-1}): 2090 ($-N_3$ and $-C{\equiv}C-$), 1515, 1333 ($-NO_2$). ^{1}H NMR ($CDCl_3$) δ (ppm): 2.01 (s, 1H, $-C{\equiv}CH$), 2.17 (m, 2H, $-CH_2-$), 2.51 (t, 2H, J = 6.6 Hz, $-CH_2-$), 3.60 (t, J = 5.7 Hz, 4H, $-N-CH_2-$), 3.72 (t, J = 6.0 Hz, 4H, N_3-CH_2-), 4.46 (t, J = 6.0 Hz, 2H, $-CH_2-O-$), 6.80 (d, 2H, J = 9.0 Hz, ArH), 7.67 (d, J = 8.7 Hz, 2H, ArH), 7.92 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$) δ (ppm): 15.4, 28.2, 49.0, 51.0, 68.3, 68.5, 69.5, 83.4, 109.4, 109.7, 112.2, 116.8, 117.7, 126.4, 145.5, 147.2, 148.8, 149.9, 155.5.

General Procedure for Synthesis of HP1 and HP2. HP1 and **HP2** were synthesized by the Cu-catalyzed 1,3-dipolar cycloadditions from chromophore **M1** and **M2**, respectively. A typical experimental procedure for the preparation of **HP1** is given below as an example.

Chromophore **M1** (56 mg, 0.12 mmol) was dissolved in DMF (6 mL) under nitrogen, and then an aqueous solution of $CuSO_4$ (150 μL, 0.04 M) and sodium ascorbate (NaAsc) (150 μL, 0.08 M) was dropped. After the reaction was stirred for 10 h at room temperature, the end-capped chromophore **4** (55 mg, 0.13 mmol) was added; at the same time, another batch of $CuSO_4$ (50 μL, 0.04 M) and NaAsc (50 μL, 0.08 M) was also added. The reaction mixture continued to stir for 9 h. After that, a lot of methanol was poured into the mixture and then filtered. The obtained solid was further purified by reprecipitation from its DMF solution into methanol to afford an orange-red powder (85 mg, 84.2%). $M_w = 4.26 \times 10^5$, $M_w/M_n = 1.22$ (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 1299, 1130 ($-SO_2$). ^{1}H NMR (DMSO-d_6) δ (ppm): 0.9−1.2 ($-CH_3$), 1.6−1.9 ($-CH_2-$), 2.6−2.8 ($-CH_2-$), 3.3 ($-SO_2CH_2-$), 3.4 ($-N-CH_2-$), 3.6−3.8 ($-N-CH_2-$), 4.3−4.5 ($-N-CH_2-$), 6.6−6.8 (ArH), 7.6−8.0 (ArH). ^{13}C NMR (DMSO-d_6) δ (ppm): 11.9, 12.8, 18.8, 23.1, 24.0, 44.2, 46.1, 46.4, 47.2, 54.2, 55.8, 111.5, 112.2, 122.8, 123.1, 126.1, 126.5, 129.5, 138.7, 139.5, 143.1, 144.2, 146.2, 151.0, 151.6, 156.0, 156.4. UV−vis (THF, 0.02 mg/mL): λ_{max} (nm): 445.

HP2. Chromophore **M2** (69 mg, 0.15 mmol), **5** (62 mg, 0.17 mmol). After the reaction was stirred 24 h, the end-capped group **5** was added for the next 9 h reaction. Red powder (101 mg, 80.8%). $M_w = 2.59 \times 10^5$, $M_w/M_n = 1.57$ (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 2095 ($-N_3$), 1515, 1340 ($-NO_2$). ^{1}H NMR ($CDCl_3$) δ (ppm): 1−1.4 ($-CH_3$), 2.0−2.4 ($-CH_2-$), 2.6−3.0 ($-CH_2-$), 3.1−4.6 ($-N-CH_2-$), 6.3−6.8 (ArH), 7.3−8.0 (ArH). ^{13}C NMR (DMSO-d_6) δ (ppm): 13.0, 22.0, 29.0, 31.1, 35.0, 44.8, 47.2, 48.5, 50.5, 69.1, 109.8, 111.7, 112.4, 116.8, 117.5, 123.4, 125.6, 126.2, 126.6, 136.0, 139.8, 143.8, 144.7, 146.9, 148.4, 151.1, 155.3. UV−vis (THF, 0.02 mg/mL): λ_{max} (nm): 464.

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 spin-coated onto indium−tin oxide (ITO)-coated glass substrates, which were cleaned by *N*,*N*-dimethyformide, acetone, distilled water, and THF sequentially in 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 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: 7.7 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 compounds **1**−**3** was shown in Scheme S1, and the detailed procedure was similar as reported in the literature and our previous case.[15] Then, under the normal azo coupling reaction conditions, especially at the low reaction temperature (0 °C), monomers **M1** and **M2** could be easily obtained with satisfied yields. From the structure of **M1** and **M2**, it was easily seen that both of the azido and yne groups were present, and these two reactive groups possessed high reactivity and could react with each other at temperatures a little higher than room temperature. That is to say, if the two monomers, **M1** and **M2**, were prepared through other approaches, perhaps we could not obtain the two monomers due to the high reactivity of azido and alkyne groups. Thus, the usage of the two diazonium salts, **1** and **3**, possessed at least two advantages: (1) the followed azo coupling reaction could be conducted in pure organic solvent, avoiding the general used inorganic acids and the possible low solubility of the reaction starting materials in the mixed solvent of organic solvent and water under the normal azo coupling reactions; (2) the high reactivity of the diazonium salts assured the high yields of the azo coupling reaction at low temperature, at which both of the azido and alkyne groups are stable. Thus, the successful preparation of monomers containing both of the azido and alkyne groups might give light on the syntheses of other monomers with different functionalities. Actually, the obtained two monomers, **M1** and **M2**, were relatively stable under normal storage conditions: at 25 °C, they remained unchanged for nearly 1 month. So, for the preparation of other monomers containing both of the azido and alkyne groups, the reaction temperature might be raised to 25 °C, but not only 0 °C used in our case.

The polymerization process of **M1** and **M2** was handled very carefully. As mentioned in the Introduction, the previous literatures have proposed that the Cu(I)-catalyzed click polymerizations of the AB_2 monomers failed to yield soluble polymers due to the self-oligomerization. After the successful utilization of the Sharpless "click" reaction in the linear polymeric systems,[12b,c,f] we considered that the "click" reaction might be controlled by adjusting the synthetic procedure. Thus, we attempted to prepare hyperbranched polymers from AB_2 monomers through the Sharpless "click" reaction. Also, we thought that after the termination of the polymerization process there should be some unreacted azido groups remained, which could react with the remaining alkyne moieties, directly leading to the final products insoluble during the purification process; even the yielded polymer was soluble at the moment of the termination of polymerization. To avoid this possible cross-linking reaction, we would like to introduce some molecules with similar structure but only containing alkyne groups as monomers to react with the possible unreacted azido ones at the second stage of the polymerization process. This strategy was often used in the preparation of hyperbranched polymers through other reactions, for example, Suzuki reactions,[16] though not being applied to the stuff of the click chemistry. Therefore, as described in the Experimental Section, chromophore **4** or **5** was added to the polymerization reaction to react with the unreacted azido moieties. At the same time, another batch of catalysts was added to aid the followed click reaction between the formed reactive hyperbranched polymer intermediate and chromophore **4** or **5**, since the previous added catalyst might still coordinate with the azido and yne groups in the formed hyperbranched polymer intermediate. As presented in the Experimental Section, the second added batch of catalysts was not the same as the first one, but much less (1/3). Actually, we have tried to add the same quantity, but no soluble hyperbranched polymer was yielded and only insoluble cross-linked polymer was obtained. We thought that the possible reason might be the too high concentration of catalysts, which further accelerated the polymerization reaction of the reactive hyperbranched polymer intermediate, leading to the cross-linked insoluble polymer. Thus, we added less amounts of catalysts (1/3 of the original one). Fortunately, the click reaction worked well this time, and soluble hyperbranched polymers, **HP1** and **HP2**, were prepared successfully. This was understandable. Under high concentration of catalysts, not only the click reaction between the formed reactive hyperbranched polymer intermediate and chromophore **4** or **5** but also that in the reactive hyperbranched polymer intermediate itself were accelerated rapidly. And the latter one resulted in the unexpected insoluble products. However, while the concentration of catalysts decreased, the catalysts would first coordinate with chromophore **4** or **5** due to relatively higher concentration of chromophore **4** or **5** in comparison with the coordination points in the reactive hyperbranched polymer intermediate. After this, the concentration of catalysts was even lower, which would have little influence on the click reaction of the formed reactive hyperbranched polymer intermediate. Thus, with the decreased amount, the second batch of catalysts would mainly accelerate the click reaction between chromophore **4** or **5** and the formed reactive hyperbranched polymer intermediate to give soluble hyperbranched polymers with no azido groups.

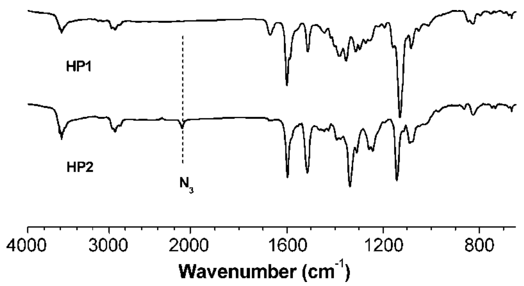


Figure 1. IR spectra of polymers **HP1** and **HP2**.

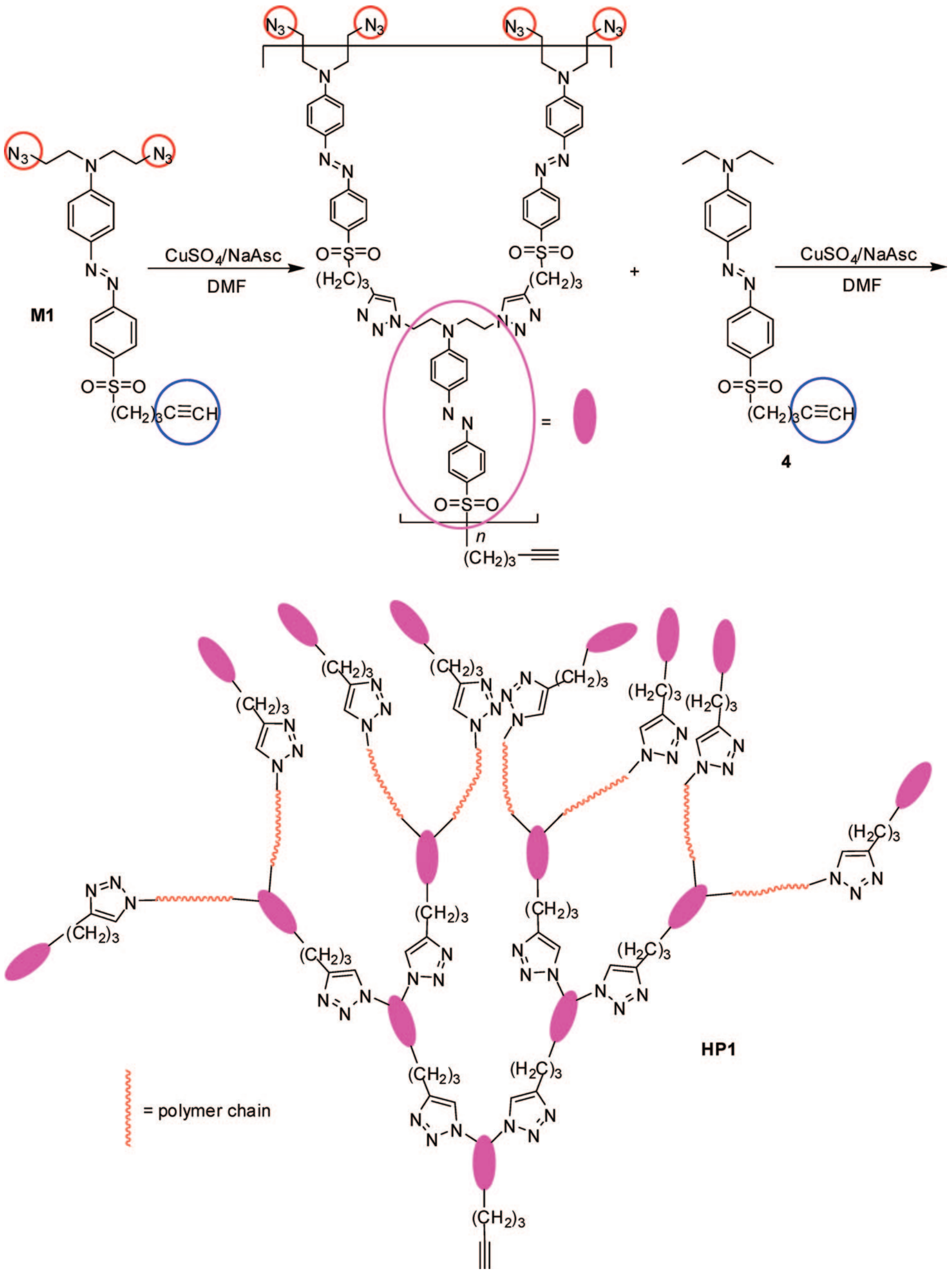
Thus, by modifying the synthetic procedure, soluble hyperbranched polymers, **HP1** and **HP2**, could be obtained conveniently from AB_2 momomers via click chemistry under copper(I) catalysis. The successful examples demonstrated here would benefit the construction of hyperbranched polymers from AB_2 momomers through click chemistry reaction, and many other functional hyperbranched ones could be prepared. Also, it might be possible to obtain the corresponding soluble hyperbranched polymers from the previous reported AB_2 momomers in the literature, which failed to give soluble products, by modifying the synthetic procedure carefully.

Structural Characterization. The monomers and polymers were characterized by spectroscopic methods, and all gave satisfactory spectral data. The NLO chromophores **M1** and **M2** were new compounds, and the two hyperbranched polymers **HP1** and **HP2** were not reported yet. Figure 1 shows the IR spectra of **HP1** and **HP2**, in which the absorption bands associated with the nitro groups were at about 1515 and 1340 cm^{-1} in **HP2**, while that of sulfonyl group at about 1299 and 1130 cm^{-1} in **HP1**. In comparison with the IR spectra of **M1** and **M2** (Figure S1), no absorption band at about 2095 cm^{-1} was found in the spectrum of **HP1**, confirming that no azido and yne moieties were present. However, it was easily seen that there was a weak absorption at about 2095 cm^{-1} in the spectrum of **HP2**, indicating that there were still some azido groups present without the click reaction with the added chromophore **5**.

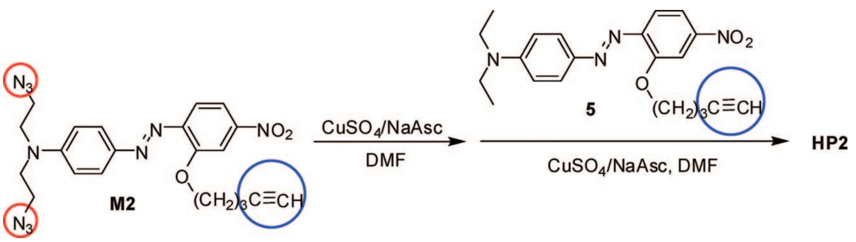
In the preparation procedure, the whole process of the click reaction was monitored by IR spectra, and only when the absorption peak of the azido and yne groups at about 2095 cm^{-1} disappeared, the reaction was then stopped. And actually, during the synthesis of **HP2**, no peak of the azido groups was observed in the IR spectrum of the reaction mixture, when the reaction was stopped. However, the weak absorption of the azido groups was found in the spectrum of **HP2**. This should be caused by the low concentration of azido groups in the reaction mixture we monitored. Although **HP2** contained some unreacted azido groups, it was very stable during the storage and characterization process, indicating that a small amount of azido moieties would not lead to the cross-linking reaction of the hyperbranched polymers, since the azido moieties were surrounded by other bulky groups in the polymers.

The ^{1}H NMR spectra of hyperbranched polymers **HP1** and **HP2** and their corresponding monomers **M1** and **M2** are

Scheme 2



Scheme 3



shown in Figures S2−S7. The chemical shifts were consistent with the proposed polymer structure as demonstrated in Schemes 2 and 3. In comparison with their corresponding monomers, there were some new peaks which appeared in the ^{1}H NMR spectra of **HP1** and **HP2**. For example, the peaks around 1.0 ppm should be ascribed to the signal of the methyl groups, which were derived from chromophore **4** or **5**, indicating that the polymerization process really underwent as demonstrated in Schemes 2 and 3. The obtained ^{13}C NMR data of **HP1** and **HP2** further confirmed the above points; for example, the signal of the carbon atoms in triple bonds disappeared completely. Also, the data of ^{13}C NMR coincided with the previous reported cases and demonstrated that the copper(I)-catalyzed click reactions offered control of the regiochemistry at the [1,2,3]-triazole ring, resulting only in 1,4-disubstituted [1,2,3]-triazoles.[1a,5b]

The molecular weights of **HP1** and **HP2** were determined by gel permeation chromatography (GPC) with DMF as an eluent and polystyrene standards as calibration standards. As

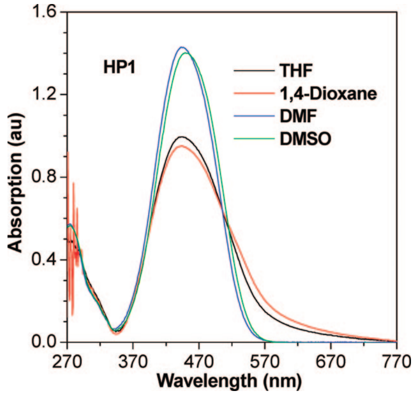


Figure 2. UV−vis spectra of **HP1** in different solvents (0.02 mg/mL).

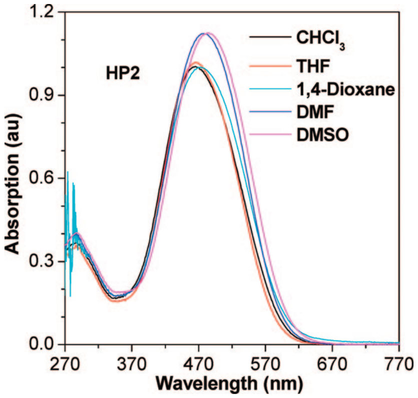


Figure 3. UV−vis spectra of **HP2** in different solvents (0.02 mg/mL).

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

	$CHCl_3$	THF	1,4-dioxane	DMF	DMSO	film
HP1	(461)	445 (453)	442 (448)	443 (464)	449 (474)	434
HP2	465 (502)	464 (491)	470 (485)	475 (506)	484 (512)	468

[a] The maximum absorption wavelength of polymer solutions with the concentrations fixed at 0.02 mg/mL, while the maximum absorption wavelength of the corresponding small chromophore molecules **4** or **5** in diluted solutions (1.25×10^{-5} mol/mL) is given in parentheses.

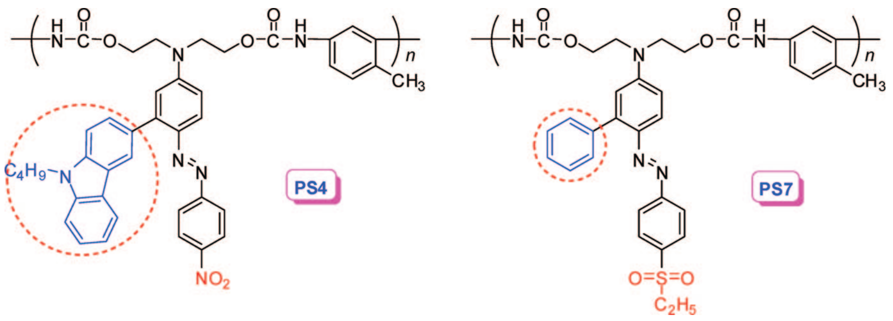
shown in Table 1 and the Experimental Section, the two hyperbranched polymers possessed high molecular weight, indicating that the polymerization method reported here was successful to construct hyperbranched polymeric structure with high molecular weight and good solubility from AB_2 monomers through the click reaction. The polymers were thermally stable. Their TGA thermograms are shown in Figure S8, and the 5% weight loss temperature of polymers are listed in Table 1. **HP1** exhibited better thermal stability than **HP2**, possibly due to its higher molecular weight. The glass transition temperatures (T_g) of **HP1** and **HP2** were investigated using a differential scanning calorimeter (Table 1), and they have moderate T_gs, 132 and 117 °C, respectively.

UV−vis Spectra and Site-Isolation Effects. HP1 and **HP2** were soluble in common organic solvents such as THF, 1,4-dioxane, DMF, and DMSO. The UV−vis absorption spectra of the polymers in different solvents are demonstrated in Figures 2 and 3, while the maximum absorption wavelengths (λ_{max}) of chromophores **4** and **5** are shown in Table 2. It was easily seen that the chromophore moieties in **HP1** and **HP2** exhibited blue-shifted maximum absorption in comparison with those of the free chromophores in the same solvent (Table 2). In **HP1** and **HP2**, the chromophore moieties were surrounded by [1,2,3]-triazole rings formed during the polymerization process, which might act as isolation moieties. Generally, 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.[17] Thus, the abnormal UV−vis absorption behavior of **HP1** and **HP2** should disclose that the chromophore moieties in them were surrounded by the isolation groups, which shielded the chromophore moieties from the solvatochomic effect. That is to say, in the two hyperbranched polymers, the effective site isolation effect was achieved, which would directly reduce the strong intermolecular dipole−dipole interactions between chromophore moieties and benefit the ordered noncentrosymmetric alignment during the poling process.

As shown in Figure 2, the difference of the maximum absorption wavelengths of **HP1** in different solvents was very little, not larger than 7 nm (in 1,4-dioxane and DMSO), demonstrating the effective site isolation effect. However, the case in **HP2** was not the same; the difference was as large as 20 nm (in THF and DMSO). But except for DMSO, the difference of the maximum absorption wavelengths of **HP2** in different solvents was not so large, and less than the difference of the free chromophore **5** (11 nm vs 21 nm in 1,4-dioxane and DMF), indicating the presence of the site isolation effect. The different disclosed site isolation behavior in **HP1** and **HP2** should be caused by the different structure: in **HP1**, the isolation groups were on the two terminal side of the chromophore moieties; while in **HP2**, one isolation group was linked to the π-conjugated bridge, and the nitro groups were exposed outside to facilitate the possible interaction between the chromophore moieties. Thus, to achieve more effective site isolation effect, the isolation moieties should be placed at both of the donor and acceptor sides, as in the case of **HP1**. The maximum absorption wavelengths of **HP1** and **HP2** in solid films were also measured (Table 2); these two polymers still exhibited much blue-shifted maximum absorption wavelengths. This would lead to good transparency and reduced optical loss in devices, which would surely benefit their practical application in the photonic fields.

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. The method for the calculation of the SHG coefficients (d_{33}) for the poled films has been reported in our previous papers.[12] From the experimental data, the d_{33} values of **HP1** and **HP2** were calculated to be 77.9 and 124.4 pm/V, respectively, at 1064 nm fundamental wavelength (Table 1). To check the reproducibility, we repeated the measurements three times and got the same results. The values were relatively high for polymers containing this kind of azo-chromophore moieties, especially for **HP2**. In comparison with the values of other polymers containing similar azo-chromophores tested by the same equipment, the d_{33} values of **HP1** and **HP2** were still very high. Previously, we have prepared a series of azo-chromophore-containing polyurethanes (**PS1**−**PS8**, Chart S1),[12a] in which the size of the isolation groups was changed from very small (hydrogen atoms) to larger (carbazolyl ones), and the macroscopic NLO effects could be boosted much higher when the isolation group was the carbazolyl one in **PS4** (82.3 pm/V) and the phenyl one in **PS7** (63.0 pm/V) (Chart 1). Here, in **HP1** and **HP2**, the size of the isolation groups, triazole moieties, was smaller than both of the carbazolyl and phenyl ones in **PS4** and **PS7**, but the tested NLO effects were much higher than those of **PS4** and **PS7**. This should be ascribed to two possible reasons: (1) The special dendrimer-like structure of

Chart 1



hyperbranched polymers, such as the globular structure, the three-dimentional spatial separation of the chromophore moieties, which facilitated the noncentrosymmetric alignment of chromophore moieties under the electric field. (2) There were three triazole rings surrounded the azo-chromophore groups in **HP1** and **HP2**, which could decrease the strong intermolecular dipole−dipole interactions of chromophore moieties more efficiently, benefiting the followed poling-induced noncentrosymmetric alignment, according to the site isolation principle.

As discussed above concerning the UV−vis spectra of **HP1** and **HP2**, the three triazole moieties formed in the click polymerization process were important to achieve more effective site isolation, which directly contributed to the large NLO effects. Thus, the above-mentioned reason 2 should account for the good results of **HP1** and **HP2**. On the other hand, in our previous case of NLO hyperbranched polymers, the hyperbranched polymers (**PS9**, Chart S2) demonstrated better macroscopic NLO property over its corresponding linear analogue (**PS10**, Chart S3),[14a] which was due to the special structure and several advantages of hyperbranched polymers. That is to say, the unique structure of hyperbranched polymers contributed to the enhanced NLO effects of NLO hyperbranched polymers. Therefore, both of the above two points were the reasons for the good NLO properties of **HP1** and **HP2**.

In comparison with another series of hyperbranched polymers with similar structure (**PS11**−**13**, Chart S4), **HP1** still demonstrated larger NLO effects, indicating that there was still a "suitable isolation group" present in the hyperbranched polymer system, just as we proposed in the linear polymer system,[12] if we did not consider the preparation procedure for, and different real structure of, **HP1** and **PS11**−**13**. Thus, it was suggested that to construct NLO hyperbranched polymer with even better macroscopic NLO effects, the size and properties of isolation groups between the chromophore moieties in the final products should be considered, in addition to the preparation procedure and the degree of branching. Further work was still needed to confirm this point.

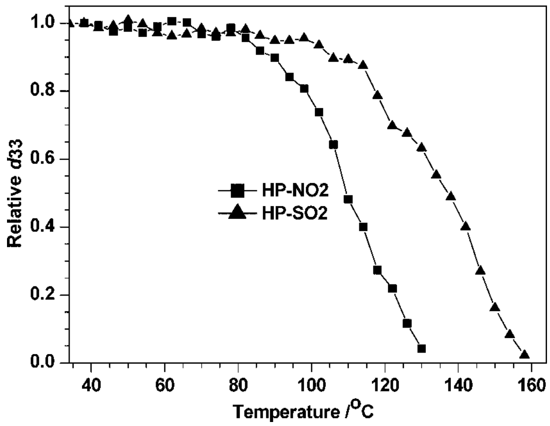


Figure 4. Decay curves of SHG coefficient of HB-NO_2 and HB-SO_2 as a function of temperature.

Considering there might be some resonant enhancement due to the absorption of the chromophore moieties at 532 nm, the NLO properties of **HP1** and **HP2** should be smaller as shown in Table 1 ($d_{33}(\infty)$), which were calculated by using the approximate two-level model. However, the $d_{33}(\infty)$ values of **HP1** and **HP2** were still higher than other linear polymers containing similar azo-chromophore moieties. To further explore the alignment of the chromophore moieties in the polymers, we measure their order parameter (Φ). Figures S9 and S10 demonstrated the UV−vis spectra of the film of **HP1** and **HP2** before and after corona poling. It was easily seen that after the corona poling the dipole moments of the chromophore moieties in the polymers were aligned and the absorption curves decreased due to birefringence. From the absorption change, the Φ values for the polymers could be calculated according to the equation presented in Table 1 (footnote h), which were still relatively high, further showing the good alignment of chromophore moieties in **HP1** and **HP2**. Thus, the larger calculated $d_{33}(\infty)$ and Φ values of **HP1** and **HP2** confirmed the mentioned advantages of hyperbranched polymers again, indicating that NLO hyperbranched polymers could be considered as promising candidates for the practical photonic applications.

The dynamic thermal stabilities of the NLO activities of the polymers were investigated by depoling experiments, in which the real-time decays of their SHG signals were monitored as the poled films were heated from 35 to 180 °C in air at a rate of 4 °C/min. Figure 4 shows the decay of SHG coefficient of **HP1** and **HP2** as a function of temperature; the onset temperatures for decays were found to be 118 and 93 °C. The results indicated that the long-term temporal stability of the polymers was relatively good, and the better performance of **HP1** should be ascribed to its higher T_g.

Conclusion

In summary, we have successfully synthesized two new azo-chromophore-containing hyperbranched polytriazoles derived from AB_2 monomers via click chemistry under copper(I) catalysis by modifying the synthetic procedure. The two polymers were soluble in organic solvents and demonstrated higher macroscopic NLO effects, in comparison with their linear analogues containing the chromophores with similar structure. Thus, coupled with their good thermal stability, they were promising candidates for the practical photonic applications. And the approach to hyperbranched polymers through click chemistry reactions presented here might shed light on the preparation of many other functional hyperbranched polymers.

Acknowledgment. We are grateful to the National Science Foundation of China (No. 20674059), the National Fundamental Key Research Program, and Hubei Province for financial support.

Supporting Information Available: Synthetic details of some compounds; IR, NMR, and TGA spectra; UV−vis spectra of the polymer films; structures of some analogues. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596–2599. (b) Helms, B.; Mynar, J. L.; Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 15020–15021. (c) Binder, W. H.; Sachsenhofer, R. *Macromol. Rapid Commun.* **2007**, *28*, 15–54. (d) Lutz, J. F. *Angew. Chem., Int. Ed.* **2007**, *46*, 1018–1025. (e) Ornelas, C.; Aranzaes, J. R.; Cloutet, E.; Alves, S.; Astruc, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 872–877. (f) Qin, A.; Jim, C. K. W.; Lu, W.; Lam, J. W. Y.; Häussler, M.; Dong, Y.; Sung, H. H. Y.; Williams, I. D.; Wong, G. K. L.; Tang, B. Z. *Macromolecules* **2007**, *40*, 2308–2317. (g) Gao, H.; Louche, G.; Sumerlin, B. S.; Jahed, N.; Golas, P.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 8979–8982. (h) Sumerlin, B. S.; Tsarevsky, N. V.; Louche, G.; Lee, R. Y.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 7540–7545. (i) Lutz, J. F.; Börner, H. G.; Weichenhan, K. *Macromol. Rapid Commun.* **2005**, *26*, 514–518.

(2) (a) Wu, P.; Feldman, A. K.; Nugent, A. K.; Hawker, C. J.; Scheel, A.; Voit, B;.; Pyun, J.; Fréchet, J. M. J.; Sharpless, K. B.; Fokin, V. V. *Angew. Chem., Int. Ed.* **2004**, *43*, 3928–3932. (b) Li, C.; Finn, M. G. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5513–5515. (c) Diaz, D. D.; Punna, S.; Holzer, P.; Mcpherson, A. K.; Sharpless, K. B.; Fokin, V. V.; Finn, M. G. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *42*, 4392–4403. (d) Binder, W. H.; Kluger, C. *Macromolecules* **2004**, *37*, 9321–9330. (e) Bock, V. D.; Hiemstra, H.; van Maarseveen, J. H. *Eur. J. Org. Chem.* **2006**, 51–68. (f) Sawa, M.; Hsu, T.-L.; Itoh, T.; Sugiyama, M.; Hanson, S. R.; Vogt, P. K.; Wong, C.-H. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 12371–12376. (g) Altintas, O.; Hizal, G.; Tunca, U. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5699–5706. (h) Li, H.; Cheng, F.; Duft, A. M.; Adronov, A. *J. Am. Chem. Soc.* **2005**, *127*, 14518–14524. (i) Itsuno, S. *Prog. Polym. Sci.* **2005**, 540–558.

(3) (a) O'Reilly, R. K.; Joralemon, M. J.; Hawker, C. J.; Wooley, K. L. *New J. Chem.* **2007**, *31*, 718–724. (b) Malkoch, M.; Schleicher, K.; Drockenmuller, E.; Hawker, C. J.; Russell, T. P.; Wu, P.; Fokin, V. V. *Macromolecules* **2005**, *38*, 3663–3678. (c) Binder, W. G.; Sachsenhofer, R. *Macromol. Rapid Commun.* **2008**, *29*, 952–981. (d) Bu, H.-B.; Götz, G.; Reinold, E.; Vogt, A.; Schmid, S.; Blanco, R.; Segurab, J. L.; Bäuerle, P. *Chem. Commun.* **2008**, 1320–1322. (e) Meldal, M.; Tornøe, C. W. *Chem. Rev.* **2008**, *108*, 2952–3015. (f) Campos, L. M.; Meinel, I.; Guino, R. G.; Schierhorn, M.; Gupta, N.; Stucky, G. D.; Hawker, C. J. *Adv. Mater.* **2008**, *20*, 3728–3733. (g) Codelli, J. A.; Baskin, J. M.; Agard, N. J.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2008**, *130*, 11486–11493. (h) Shen, X.; Liu, H.; Li, Y.; Liu, S. *Macromolecules* **2008**, *41*, 2421–2425.

(4) (a) O'Reilly, R. K.; Joralemon, M. J.; Wooley, K. L.; Hawker, C. J. *Chem. Mater.* **2005**, *17*, 5976–5988. (b) Lau, K.-N.; Chow, H.-F.; Chan, M.-C.; Wong, K.-W. *Angew. Chem., Int. Ed.* **2008**, *47*, 6912–6916. (c) Tasdelen, M. A.; Camp, W. V.; Goethals, E.; Dubois, P.; Prez, F. D.; Yagci, Y. *Macromolecules* **2008**, *41*, 6035–6040. (d) Johnson, J. A.; Finn, M. G.; Koberstein, J. T.; Turro, N. J. *Macromol. Rapid Commun.* **2008**, *29*, 1052–1072. (e) Fleischmann, S.; Komber, H.; Voit, B. *Macromolecules* **2008**, *41*, 5255–5264. (f) Eugene, D. M.; Grayson, S. M. *Macromolecules* **2008**, *41*, 5082–5084. (g) Rengifo, H.; Chen, L.; Grigoras, C.; Ju, J.; Koberstein, J. T. *Langmuir* **2008**, *24*, 7450–7456.

(5) (a) Qin, A.; Lam, J. W. Y.; Jim, C. K. W.; Zhang, L.; Yan, J.; Haäussler, M.; Liu, J.; Dong, Y.; Liang, D.; Chen, E.; Jia, G.; Tang, B. Z. *Macromolecules* **2008**, *41*, 3808–3822. (b) Scheel, A. J.; Komber, H.; Voit, B. I. *Macromol. Rapid Commun.* **2004**, *25*, 1175–1180.

(6) (a) Zyss, J. *Molecular Nonlinear Optics: Materials, Physics and Devices*; Academic Press: Boston, 1994. (b) Chemla, D. S.; Zyss, J. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: Orlando, FL, 1987; Vol. 1. (c) Zyss, J. *Nonlinear Opt.* **1991**, *1*, 3–18. (d) Ermer, S.; Valley, J. F.; Lytel, R.; Lipscomb, G. F.; Vaneck, T. E.; Girton, D. G. *Appl. Phys. Lett.* **1992**, *61*, 2272. (e) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; John Wiley & Sons: New York, 1991. (f) Dalton, L. R. *Chem. Ind.* **1997**, *7*, 510–514. (g) Sandhya, K. Y.; Pillai, C. K. S.; Tsutsumi, N. *Prog. Polym. Sci.* **2004**, *29*, 45–74. (h) Lee, J. Y.; Bang, H. B.; Park, E. J.; Baek, C. S.; Rhee, B. K.; Lee, S. M. *Synth. Met.* **2004**, *144*, 159–167.

(7) (a) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int, Ed. Engl.* **1995**, *34*, 155–173. (b) Marder, S. R.; Kippelen, B.; Jen, A. K. Y.; Peyghambarian, N. *Nature (London)* **1997**, *388*, 845–851. (c) Bai, Y.; Song, N.; Gao, J. P.; Sun, X.; Wang, X.; Yu, G.; Wang, Z. Y. *J. Am. Chem. Soc.* **2005**, *127*, 2060–2061. (d) Andreu, R.; Blesa, M. J.; Carrasquer, L.; Garin, J.; Orduna, J.; Villacampa, B.; Alcala, R.; Casado, J.; Delgado, M. C. R.; Navarrete, J. T. L.; Allain, M. *J. Am. Chem. Soc.* **2005**, *127*, 8835–8845. (e) Wang, Q.; Wang, L. M.; Yu, L. P. *Macromol. Rapid Commun.* **2000**, *21*, 723–745.

(8) (a) Lee, M.; Katz, H. E.; Erben, C.; Gill, D. M.; Gopalan, P.; Heber, J. D.; McGee, D. J. *Science* **2002**, *298*, 1401–1403. (b) Shi, Y.; Zhang, C.; Zhang, H.; Bechtel, J. H.; Dalton, L. R.; Robinson, B. H.; Steier, W. H.; Dalton, L. R. *Science* **2000**, *288*, 119–122. (c) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31–75. (d) Ma, H.; Jen, A. K. Y. *Adv. Mater.* **2001**, *13*, 1201–1205. (e) Moerner, W. E.; Jepsen, A. G.; Thompson, C. L. *Annu. Rev. Mater. Sci.* **1997**, *27*, 585–623. (f) Barclay, G. G.; Ober, C. K. *Prog. Polym. Sci.* **1993**, *18*, 899–945.

(9) (a) Jang, S.-H.; Luo, J.; Tucker, N. M.; Leclercq, A.; Zojer, E.; Haller, M. A.; Kim, T.-D.; Kang, J.-W.; Firestone, K.; Bale, D.; Lao, D.; Benedict, J. B.; Cohen, D.; Kaminsky, W.; Kahr, B.; Bredas, J.-L.; Reid, P.; Dalton, L. R.; Jen, A. K.-Y. *Chem. Mater.* **2006**, *18*, 2982–2988. (b) Marder, S. R.; Cheng, L. T.; Tiemann, B. G.; Friedli, A. C.; Blanchard-Desce, M.; Perry, J. W.; Skindhøj, J. *Science* **1994**, *263*, 511–514. (c) Kim, T. D.; Luo, J.; Tian, Y.; Ka, J. W.; Tucker, N. M.; Haller, M.; Kang, J. W.; Jen, A. K. Y. *Macromolecules* **2006**, *39*, 1676–1680. (d) Luo, N.; Wang, D. N.; Ying, S. K. *Macromolecules* **1997**, *30*, 4405–4409. (e) Suresh, S.; Gulotty, R. J.; Bales, S. E.; Inbasekaran, M. N.; Chartier, M. A.; Cummins, C.; Smith, D. W. *Polymer* **2003**, *44*, 5111–5117.

(10) (a) Robinson, B. H.; Dalton, L. R. *J. Phys. Chem. A* **2000**, *104*, 4785–4795. (b) Robinson, B. H.; Dalton, L. R.; Harper, H. W.; Ren, A.; Wang, F.; Zhang, C.; Todorova, G.; Lee, M.; Aniszfeld, R.; Garner, S.; Chen, A.; Steier, W. H.; Houbrecht, S.; Persoons, A.; Ledoux, I.; Zyss, J.; Jen, A. K.-Y. *Chem. Phys.* **1999**, *245*, 35–50. (c) Dalton, L. R.; Steier, W. H.; Robinson, B. H.; Zhang, C.; Ren, A.; Garner, S.; Chen, A.; Londergan, T.; Irwin, L.; Carlson, B.; Fifield, L.; Phelan, G.; Kincaid, C.; Amend, J.; Jen, A. K.-Y. *J. Mater. Chem.* **1999**, *9*, 1905–1920. (d) Luo, J.; Haller, M.; Li, H.; Tang, H.; Jen, A. K.-Y.; Jakka, K.; Chou, C.-H.; Shu, C.-F. *Macromolecules* **2004**, *37*, 248–250. (e) Ma, H.; Liu, S.; Luo, J.; Suresh, S.; Liu, L.; Kang, S. H.; Haller, M.; Sassa, T.; Dalton, L. R.; Jen, A. K.-Y. *Adv. Funct. Mater.* **2002**, *12*, 565–574.

(11) (a) Luo, J. D.; Ma, H.; Haller, M.; Barto, R. R. *Chem. Commun.* **2002**, *8*, 888–889. (b) Kowalczyk, T. C.; Kosc, T.; Singer, K. D.; Cahill, P. A.; Seager, C. H.; Meinhardt, M. B.; Beuhler, A. J.; Wargowski, D. A. *J. Appl. Phys.* **1994**, *76*, 2505–2508. (c) Wang, F.; Harper, A. W.; Lee, M. S.; Dalton, L. R.; Zhang, H.; Chen, A.; Steier, W. H.; Marder, S. R. *Chem. Mater.* **1999**, *11*, 2285–2288.

(12) (a) Li, Z.; Li, Z.; Di, C.; Zhu, Z.; Li, Q.; Zeng, Q.; Zhang, K.; Liu, Y.; Ye, C.; Qin, J. *Macromolecules* **2006**, *39*, 6951–6961. (b) Li, Z.; Zeng, Q.; Li, Z.; Dong, S.; Zhu, Z.; Li, Q.; Ye, C.; Di, C.; Liu, Y.; Qin, J. *Macromolecules* **2006**, *39*, 8544–8546. (c) Zeng, Q.; Li, Z.; Li, Z.; Ye, C.; Qin, J.; Tang, B. Z. *Macromolecules* **2007**, *40*, 5634–5637. (d) Li, Z.; Li, P.; Dong, S.; Zhu, Z.; Li, Q.; Zeng, Q.; Li, Z.; Ye, C.; Qin, J. *Polymer* **2007**, *48*, 3650–3657. (e) Li, Z.; Dong, S.; Yu, G.; Li, Z.; Liu, Y.; Ye, C.; Qin, J. *Polymer* **2007**, *48*, 5520–5529. (f) Li, Z.; Zeng, Q.; Yu, G.; Li, Z.; Ye, C.; Liu, Y.; Qin, J. *Macromol. Rapid Commun.* **2008**, *29*, 136–141. (g) Li, Q.; Li, Z.; Zeng, F.; Gong, W.; Li, Z.; Zhu, Z.; Zeng, Q.; Yu, S.; Ye, C.; Qin, J. *J. Phys. Chem. B* **2007**, *111*, 508–514. (h) Li, Q.; Li, Z.; Ye, C.; Qin, J. *J. Phys. Chem. B* **2008**, *112*, 4928–4933. (i) Li, Q.; Yu, G.; Huang, J.; Liu, H.; Li, Z.; Ye, C.; Liu, Y.; Qin, J. *Macromol. Rapid Commun.* **2008**, *29*, 798–803. (j) Li, Z.; Dong, S.; Li, P.; Li, Z.; Ye, C.; Qin, J. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2983–2993. (k) Li, Z.; Yu, G.; Li, Z.; Liu, Y.; Ye, C.; Qin, J. *Polymer* **2008**, *49*, 901–914.

(13) (a) Fréchet, J. M. J. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4782–4787. (b) Fréchet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* **1995**, *269*, 1080–1083. (c) Fréchet, J. M. J.; Hawker, C. J.; Gitsov, I.; Leon, J. W. *J. Macromol. Sci., Pure Appl. Chem.* **1996**, *A33*, 1399–1425. (d) Hecht, S.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 74–91.

(14) (a) Zhu, Z.; Li, Z.; Tan, Y.; Li, Z.; Li, Q.; Zeng, Q.; Ye, C.; Qin, J. *Polymer* **2006**, *47*, 7881–7888. (b) Li, Z.; Qin, A.; Lam, J. W. Y.; Dong, Y.; Dong, Y.; Ye, C.; Williams, I. D.; Tang, B. Z. *Macromolecules* **2006**, *39*, 1436–1442. (c) Zhu, Z.; Li, Z.; Li, Q.; Zeng, Q.; Li, Z.; Ye, C.; Qin, J. *Chin. J. Chem.* **2007**, *25*, 237–240.

(15) (a) Starkey, E. B.; Smith, L. I.; Ungnade, H. E. *Org. Synth. Collect. Vol.* **1943**, *2*, 225. (b) Li, Z.; Qin, J.; Li, S.; Ye, C.; Luo, J.; Cao, Y. *Macromolecules* **2002**, *35*, 9232–9235. (c) Li, Z.; Huang, C.; Hua, J.; Qin, J.; Yang, Z.; Ye, C. *Macromolecules* **2004**, *37*, 371–376. (d) Li, Z.; Gong, W.; Qin, J.; Yang, Z.; Ye, C. *Polymer* **2005**, *46*, 4971–4978. (e) Li, Z.; Li, J.; Qin, J.; Qin, A.; Ye, C. *Polymer* **2005**, *46*, 363–368. (f) Li, Z.; Hua, J.; Li, Q.; Huang, C.; Qin, A.; Ye, C.; Qin, J. *Polymer* **2005**, *46*, 11940–11948. (g) Li, Z.; Li, Q.; Qin, A.; Dong, Y.; Lam, J. W. Y.; Dong, Y.; Ye, C.; Qin, J.; Tang, B. Z. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5672–5681. (h) Lee, S. J.; Lee, S. S.; Lee, J. Y.; Jung, J. H. *Chem. Mater.* **2006**, *18*, 4713–4715.

(16) (a) Liu, X. M.; Xu, J.; Lu, X.; He, C. *Org. Lett.* **2005**, *14*, 2829–2832. (b) Cao, X. Y.; Zhou, X. H.; Zi, H.; Pei, J. *Macromolecules* **2004**, *37*, 8874–8882. (c) Li, J.; Bo, Z. *Macromolecules* **2004**, *37*, 2013–2015. (d) Lai, W. Y.; Zhu, R.; Fan, Q. L.; Hou, L. T.; Cao, Y.; Huang, W. *Macromolecules* **2006**, *39*, 3707–3709.

(17) Liao, Y.; Anderson, C. A.; Sullivan, P. A.; Akelaitis, A. J. P.; Robinson, B. H.; Dalton, L. R. *Chem. Mater.* **2006**, *18*, 1062–1067.

MA8025223