

SECOND-ORDER NONLINEAR OPTICAL HYPERBRANCHED POLYMER CONTAINING ISOLATION CHROMOPHORE MOIETIES DERIVED FROM BOTH “H”-TYPE AND STAR-TYPE CHROMOPHORES*

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Abstract An NLO hyperbranched polymer (**HP1**) derived from both “H”-type and star-type chromophores was synthesized successfully for the first time with high yield *via* one-pot “A₂ + B₃” Suzuki polymerization reaction. Isolation chromophore was also introduced to further improve its performance. Although under the test conditions, the films of **HP1** could not be poled completely, it still demonstrated satisfactory macroscopic NLO effect with the second harmonic generation (SHG) coefficient *d*₃₃ value of 36 pm/V.

Keywords: Hyperbranched polymer; NLO; Isolation chromophore; “H”-type chromophore; Star-type chromophore.

INTRODUCTION

Organic/polymeric nonlinear optical (NLO) materials have continuously drawn great interest due to their several advantages that are superior to those of conventional inorganic crystal materials, such as large nonlinear optical coefficient, ultrafast response, wide response wave band, high optical damage threshold, and easy combination and modification^[1–11]. For the development of NLO materials, one of the major problems encountered is how to efficiently translate the large β values of the organic chromophores into high macroscopic NLO activities of polymers, since the strong intermolecular dipole-dipole interactions among the chromophore moieties in the polymeric system make the poling-induced noncentrosymmetric alignment of chromophores a daunting task^[12, 13]. Fortunately, an elaborate three-dimensional (3D) structure was reported to be able to minimize the dipole-dipole interactions by locking a chromophore inside the dendron shell, thus, enhance the macroscopic NLO activities by applying the site-isolation principle^[12, 14]. Due to their special 3D global highly branched structure, the dendritic NLO materials have been thus considered a very promising molecular topology for the next generation of highly efficient NLO materials^[15–18]. Hyperbranched polymers, one type of dendritic macromolecules, are of special interest because their easy synthetic accessibility, typically by one-pot syntheses, allows their production in large quantities and their application on an industrial scale^[19–26]. And actually, the hyperbranched polymers have already demonstrated their advantages in NLO material: not only NLO effect, but optical transparency, chemical and photochemical stability and compatibility in composite materials of them were also improved^[27–32].

Based on excellent results in the NLO field, we have demonstrated in dendronized polymers that the

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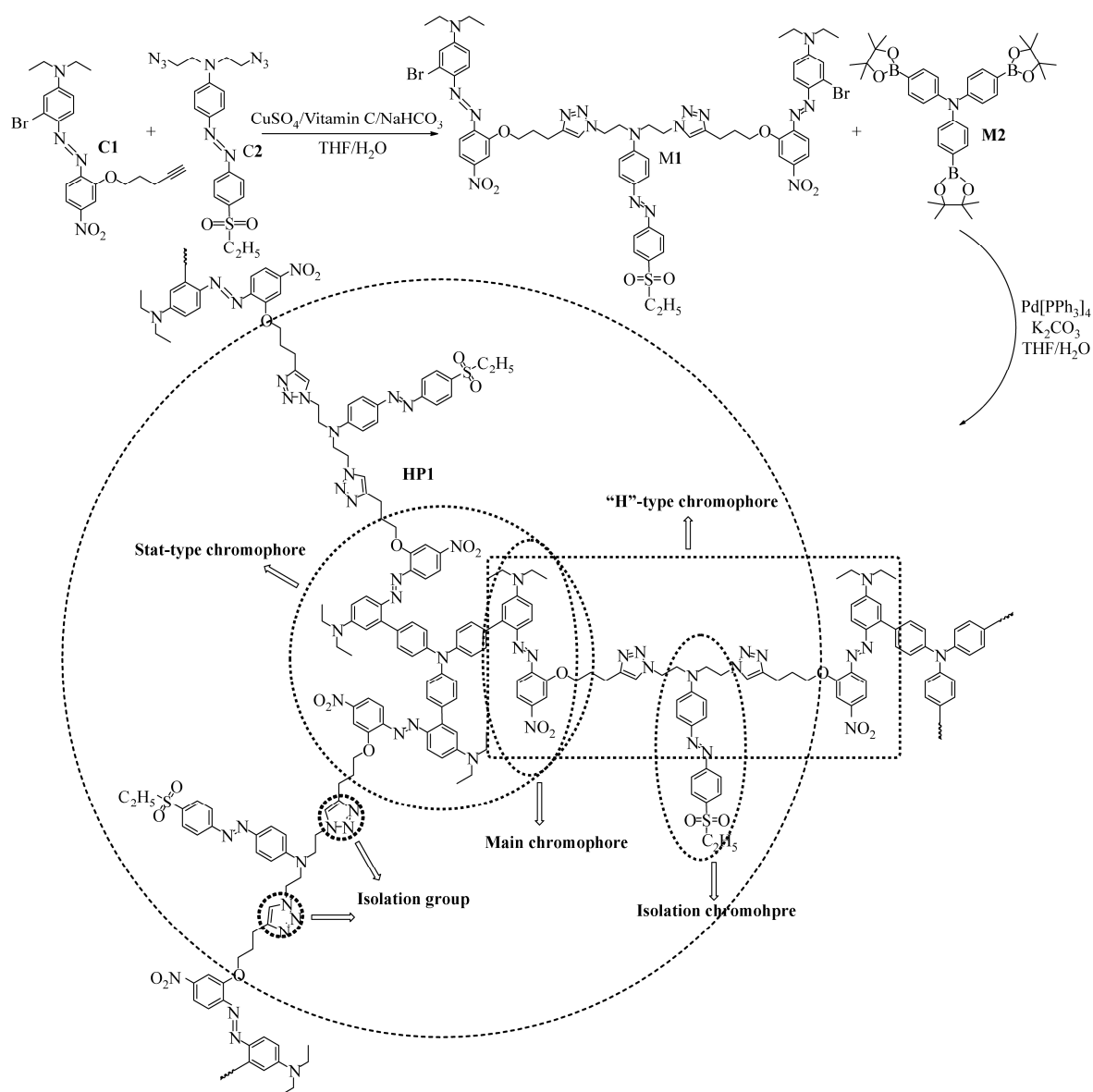
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macroscopic nonlinearity of NLO polymers could be boosted several times higher by bonding a “suitable isolation group” to the chromophore moieties^[33–39]. By applying the concept of “suitable isolation group”, the shape of chromophore was also improved from traditional rod-like structure to various other types. “H”-type^[33, 40–42] and star-type chromophores^[43, 44] were the typical examples among them. However, none of them was used in hyperbranched polymers.

On the other hand, different from normal none polar isolation groups, designed according to the site-isolation principle^[12, 14], our group recently developed a new method, isolation chromophore, to further improve the comprehensive performance of polymeric NLO materials. And this method has been already used in dendritic macromolecules, including dendrimers and hyperbranched polymers, and the results showed that their performance was improved in a large degree^[45–47]. However, the relevant example was still a little scarce, and further researches were still needed.

Therefore, in this paper, we tried to design a new NLO hyperbranched polymer **HP1** (Scheme 1), consisted



Scheme 1 Synthesis of NLO hyperbranched polymer **HP1**

of both “H”-type and star-type chromophores. Also, lower $\mu\beta$ value chromophore, sulfonyl-based one, was also introduced as isolation chromophore to improve its performance. The obtained **HP1** have good thermal stability and solubility. However, due to its too high glass transition temperature (T_g), the film of **HP1** could not be poled completely under our experimental conditions. Even so, its NLO coefficient d_{33} value was still as high as 36 pm/V. Herein, we would like to report the synthesis, characterization and optical nonlinearities of **HP1** in detail.

EXPERIMENTAL

Materials and Instrumentations

Tetrahydrofuran (THF) was dried over and distilled from K-Na alloy under an atmosphere of dry nitrogen. The B₃-type monomers **M2** and chromophores **C1** and **C2** have been already prepared in our previous work^[47]. All other reagents were used as received.

¹H- and ¹³C-NMR spectra were measured on a Varian Mercury300 spectrometer using tetramethylsilane (TMS; $\delta = 0$) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer-2 spectrometer in the region of 4000–400 cm⁻¹. UV-Visible spectra were obtained using a Shimadzu 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. THF 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 K/min in nitrogen at a flow rate of 50 cm³/min for thermogravimetric analysis (TGA). The thickness of the films was measured with an Ambios Technology XP-2 profilometer.

Synthesis of A₂-type Monomer **M1**

Chromophore **C1** (505.3 mg, 1.10 mmol), Chromophore **C2** (213.7 mg, 0.50 mmol), CuSO₄·5H₂O (10 mol%), NaHCO₃ (20 mol %) and ascorbic acid (20 mol%) were dissolved in THF (5 mL)/H₂O (1 mL) under nitrogen in a Schlenk flask. The mixture was stirred at room temperature for 3 h, then extracted with chloroform, and washed with brine. The organic layer was dried over anhydrous magnesium sulfate and purified by column chromatography using ethyl acetate/chloroform (1/1) as eluent to afford red solid **M1** (580.1 mg, 86.2%). IR (KBr), ν (cm⁻¹): 1514, 1338 (—NO₂), 1139 (—SO₂—). ¹H-NMR (300 MHz, CDCl₃, 298 K), δ (TMS): 1.23 (br, s, —CH₃, 6H), 1.31 (br, s, —CH₃, 2H), 2.25 (br, s, —CH₂—, 4H), 2.96 (br, s, —CH₂C—, 4H), 3.15 (br, s, —SCH₂—, 2H), 3.43 (br, s, —NCH₂—, 8H), 3.71 (br, s, —NCH₂—, 4H), 4.14 (br, s, —NCH₂—, 4H), 4.37 (br, s, —OCH₂—, 4H), 6.5–6.7 (m, ArH, 4H), 6.96 (s, ArH, 2H), 7.21 (s, —C=CH, 2H), 7.7–8.0 (m, ArH, 14H). ¹³C-NMR (75 MHz, CDCl₃, 298 K), δ : 7.30, 12.48, 21.72, 28.29, 44.80, 47.04, 50.54, 51.00, 68.47, 109.12, 110.76, 111.53, 114.25, 116.43, 117.77, 119.20, 122.21, 122.76, 125.79, 129.03, 131.61, 138.24, 139.90, 144.42, 146.72, 147.01, 147.93, 149.19, 151.39, 155.00. MALDI-TOF MS: calcd for (C₆₀H₆₇Br₂N₁₇O₈S): m/z [M+Na]⁺: 1369.1; found: m/z 1367.9. C₆₀H₆₇Br₂N₁₇O₈S (EA) (%), found/calcd): C, 52.99/53.53; H, 5.23/5.03; N, 17.75/17.69.

Synthesis of Hyperbranched Polymer **HP1**

A mixture of A₂-type monomer **M1** (80.8 mg, 0.06 mmol), B₃-type monomer **M2** (24.9 mg, 0.04 mmol), potassium carbonate (165.6 mg, 1.2 mmol), THF (3 mL)/water (1 mL) and a catalytic amount of Pd(PPh₃)₄ was carefully degassed and charged with argon. Then the reaction mixture was stirred at 60 °C for 8 h. Before gelation, a lot of methanol was poured into the mixture, then filtered. The obtained solid was dissolved in THF, and the insoluble solid was filtered out. After removal of the solvent, the residue was further purified by several precipitations from THF into methanol, and the obtained solid was then washed with a lot of acetone and dried in a vacuum at 40 °C to a constant weight. The resultant polymer **HP1** was obtained as red powder (63.3 mg, 73.8%). $M_w = 6340$, $M_w/M_n = 1.69$ (GPC, polystyrene calibration). IR (KBr), ν (cm⁻¹): 1514, 1338 (—NO₂), 1139 (—SO₂—). ¹H-NMR (300 MHz, CDCl₃, 298 K), δ : 0.9–1.2 (—CH₃), 2.0–2.3 (—CH₂—), 2.8–3.1 (br,

s, $-\text{CH}_2\text{C}-$ and $-\text{SCH}_2-$), 3.2–3.7 ($-\text{NCH}_2-$), 3.8 ($-\text{NCH}_2-$), 3.9–4.1 ($-\text{NCH}_2-$), 4.2–4.4 ($-\text{NCH}_2-$), 4.5–4.6 ($-\text{OCH}_2-$), 6.4–6.7 (ArH), 6.8 (ArH), 7.0–8.0 ($-\text{C}=\text{CH}$ and ArH). ^{13}C -NMR (75 MHz, CDCl_3 , 298 K), δ : 7.57, 13.03, 22.04, 28.29, 28.61, 29.88, 45.07, 47.39, 50.93, 111.55, 112.01, 116.75, 117.64, 118.42, 123.09, 123.78, 126.18, 129.41, 132.05, 134.64, 141.60, 145.79, 147.16, 147.60, 151.31, 155.38, 156.8, 161.88.

Preparation of Polymer Thin Films

The polymer was dissolved in THF (concentration *ca.* 4 wt%), and the solution was filtered through syringe filter. Polymer films were spin coated onto indium-tin-oxide (ITO)-coated glass substrates, which were cleaned by DMF, acetone, distilled water and THF sequentially in an ultrasonic bath before use. Residual solvent was removed by heating the films in a vacuum oven at 40 °C.

NLO Measurements of Poled Films

The second-order optical nonlinearity of **HP1** was determined by *in situ* second harmonic generation (SHG) experiments 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, 180 °C; voltage, 7.8 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 nitro-based chromophore **C1** containing one alkyne group and one bromine atom, the sulfonyl-based chromophore **C2** containing two azido groups and the B_3 -type monomer **M2** were synthesized in our previous work. From 2001, “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. Among them, the Cu(I)-catalyzed cycloaddition between azides and alkynes to yield triazoles was a typical “click reaction” which was first reported in 2002^[48–50]. In this work, under a typical “click reaction” between chromophores **C1** and **C2**, the A_2 -type monomer **M1** with the regular ABA structure was prepared easily. Furthermore, the formed triazoles could be utilized to act as good isolation groups between the main chromophore (the nitro-based one) and the isolation chromophore (the sulfonyl-based one)^[45, 46], according to the concept of “suitable isolation group”.

The polymerization procedure proceeded smoothly through the one-pot Suzuki coupling reaction using $\text{Pd}(\text{PPh}_3)_4$ as a catalyst, K_2CO_3 as a base and a mixture of THF/ H_2O (3/1, *V/V*) as the solvent. The copolymerization of A_2 and B_3 monomers might lead to the formation of gel rapidly, and many parameters could affect the final products in the “ $\text{A}_2 + \text{B}_3$ ” polymerization, such as temperature, reaction time, concentrations of the monomers and so on. According to our previous work on “one-pot” Suzuki hyperbranched polymerization^[51], to avoid the possible formation of gel, the concentration of A_2 -type monomer **M1** was fixed at 0.02 mmol/mL in THF. After 8 h, some insoluble red solid appeared. Thus, lots of methanol was poured into the mixture to quench the polymerization. After purification, **HP1** was obtained as a red solid in the yield of 73.8%, and the obtained polymer was readily soluble in common polar solvents, such as THF, CHCl_3 , DMF and DMSO, making their application convenient.

Characterizations

The obtained hyperbranched polymer **HP1** was characterized by spectroscopic methods, such as FTIR spectrum, NMR spectrum and so on, and all gave satisfactory data. The ^1H -NMR spectra of **HP1** and its corresponding A_2 -type monomer **M1**, which were conducted in the solvent of chloroform-*d*, are shown in Fig. 1 as an example. The chemical shifts of **M1** were consistent with the proposed polymer structure, with its characteristic peaks marked in Fig. 1. After polymerization, the peaks in the range of 7.3–7.7, assigned to the protons of ArH in

B₃-type monomer, appeared, and all the peaks showed an inclination of signal broadening obviously, indicating that the polymerizations were successful. The weight-average molecular weights of **HP1**, determined by gel permeation chromatography (GPC) with THF as an eluent and polystyrene standards as calibration standards, was tested to be 6340, with polydispersity index (PDI) of 1.69. It should, however, point out that the GPC analysis using linear polystyrenes as calibration standards often underestimates the molecular weights of hyperbranched polymers, with difference as big as *ca.* 40 times being reported in the literatures^[52–54]. The actual or true molecular weights of the **HP1** thus could be much higher than the value given by GPC. **HP1** was thermolytically resistant, with the 5% weight loss temperature (T_d) as high as 274 °C, which was investigated by thermal gravimetric analysis under an atmosphere of nitrogen. Also, its glass transition temperatures (T_g) were tested using a differential scanning calorimeter (DSC). To our surprise, its T_g value was tested as 217 °C. The high T_g value could lead high stability of the ordered dipole alignment of NLO chromophores, and surely benefit to their potential practical applications. However, it also brought out a problem, the high poling temperature, which could make the chromophores be poled unefficiently. This point would be discussed later.

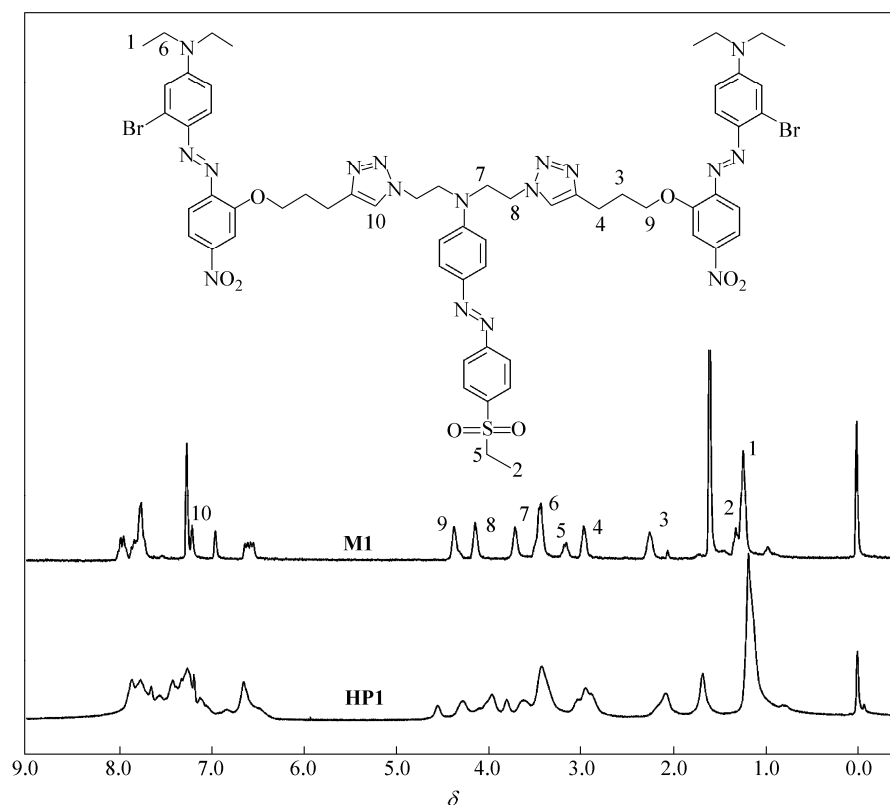


Fig. 1 ¹H-NMR spectra of hyperbranched polymer **HP1** and its corresponding monomer **M1** in chloroform-*d*

The UV-Vis absorption spectra of the hyperbranched polymer **HP1** in different solvents are demonstrated in Fig. 2. Here, an interesting phenomenon was observed. Since **HP1** consisted of two types of chromophores, and the maximum absorption wavelengths ($\lambda_{\max}$) for their π - π^* transition was not the same, there was a broad absorption in its UV-Vis spectra, which actually possessed two absorptions: one is from the nitro-based chromophore; and the other one is from the sulfonyl-based chromophore. However, the shape of this absorption peak was much different in different solvents, indicating that the solvatochromic effects to these two chromophores were different. This should be ascribed to different environment around the two types of chromophores, which also have different influences on the NLO coefficient of **HP1**.

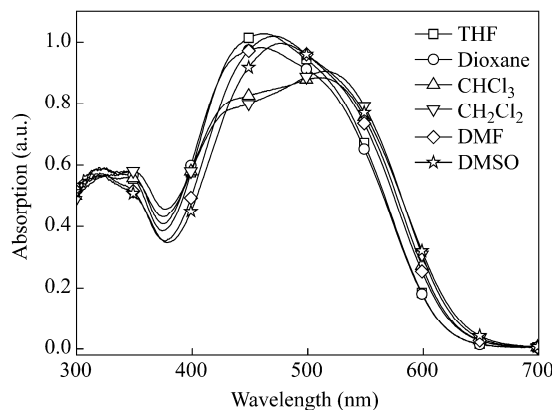


Fig. 2 UV-Vis spectra of HP1 in different solvents (0.02 mg/mL)

NLO Effect

The convenient technique to study the second-order NLO activity was to investigate the SHG processes characterized by d_{33} , an SHG coefficient. The test procedure was similar as we reported previously^[29–42], and from the experimental data, its d_{33} value was tested to be 36 pm/V, at the 1064 nm fundamental wavelength.

To be active NLO effect, the macroscopic arrangement of dipoles of NLO chromophores should be noncentrosymmetric, which was usually achieved by the poling procedure (Fig. 3): at first, a strong direct current (DC) electric field is applied to induce the reorientation of dipolar NLO chromophores in solid solutions when the thin films of the polymers are heated near or above the T_g ; and then, the films are cooled to room temperature while the electric field is still there, and the noncentrosymmetric arrangement of the dipolar NLO chromophores could be “frozen in” to form poled polymers. As mentioned above, the T_g value of **HP1** was 217 °C, and the high T_g value would require the high poling temperature, making the NLO test difficult. Thus, we can surmise that the best poling temperature of **HP1** should be around 220 °C, which was 40 °C higher than the highest poling temperature of our test conditions, thus the poling of NLO films at 180 °C may underestimate the d_{33} value dramatically, and the true or actual d_{33} value should be much higher. Even so, its d_{33} value was still tested as high as 36 pm/V, which should be attributed to its special structure: hyperbranched topological structure containing both “H”-type chromophore and star-type chromophore. Also, the isolation chromophore

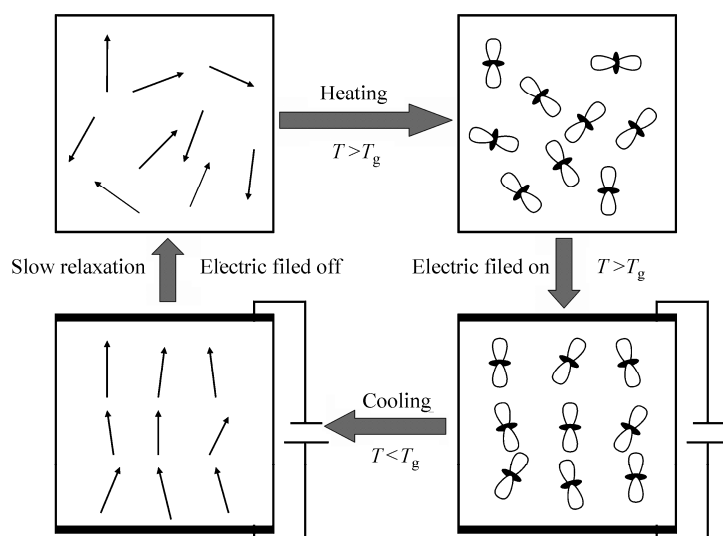


Fig. 3 The poling procedure of NLO polymers

could contribute much to the macroscopic NLO effect. However, to know more information, we must design another hyperbranched polymer with similar structure as **HP1**, but much lower T_g value. Thus, further studies were still needed.

To further study the alignment behavior of the chromophore moieties in the polymers, the order parameter (Φ) of the polymer was also measured from the change of the UV-Vis spectra of their films before and after poling under electric field, according to the equation: $\Phi = 1 - A_1/A_0$, where A_1 and A_0 are the absorbance of the polymer film after and before poling, respectively. As shown in Fig. 4, after poling, the absorbance of **HP1** decreases, indicating the chromophores in it were noncentrosymmetric. However, the shape of the absorption peak after poling was much different to that before poling, making the calculation of its accurate Φ value difficult. But this phenomenon brought out important information. As mentioned above, the absorption peak of **HP1** consists of two absorptions. Here, the different shape of the absorption peaks after and before poling might be due to the different behavior of the two type chromophores. As we know, the $\lambda_{\max}$ of nitro-based chromophore should be red-shifted than the sulfonyl-based chromophore. Thus, the blue-shifted $\lambda_{\max}$ after poling indicated that the “ Φ value” of nitro-based chromophore of **HP1** should be higher than that of sulfonyl-based chromophore. This should also confirm our idea: the higher $\mu\beta$ value chromophore was used as the main chromophore, which contributes most to the macroscopic NLO effect; the lower $\mu\beta$ value chromophore was used as the isolation chromophore, which was an isolation group between two main chromophores to decrease the dipole-dipole interactions and could be also contribute to the macroscopic NLO effect, but less than the main chromophore.

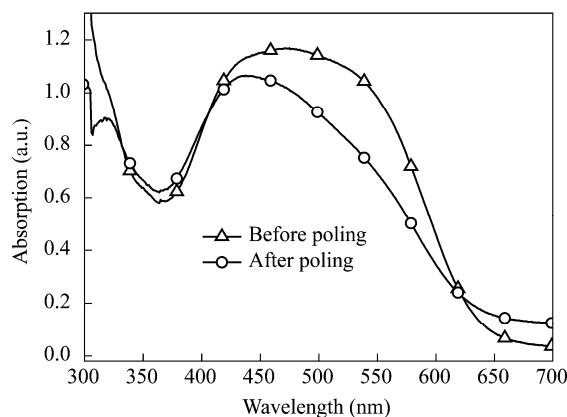


Fig. 4 Absorption spectra of **HP1** films before and after poling

CONCLUSIONS

In this paper, an NLO hyperbranched polymer **HP1** was synthesized successfully for the first time with high yield *via* one-pot “ A_2+B_3 ” Suzuki polymerization reaction. **HP1** consists of both “H”-type chromophore and star-type chromophore, as well as isolation chromophore to improve its NLO performance. Even the films of **HP1** could not be poled completely under our test conditions, the d_{33} value was still as high as 36 pm/V. Furthermore, the order parameter confirmed our previous idea of isolation chromophore.

REFERENCES

- 1 Burland, D.M., Miller, R.D. and Walsh, C.A., Chem. Rev., 1994, 94: 31
- 2 Bai, Y., Song, N., Gao, J.P., Sun, X., Wang, X., Yu, G. and Wang, Z.Y., J. Am. Chem. Soc., 2005, 127: 2060
- 3 Marks, T.J. and Ratner, M.A., Angew. Chem. Int. Ed., 1995, 34: 155

- 4 Yu, D., Gharavi, A. and Yu, L.P., *J. Am. Chem. Soc.*, 1995, 117: 11680
- 5 Marder, S.R., Kippelen, B., Jen, A.K.Y. and Peyghambarian, N., *Nature*, 1997, 388: 845
- 6 Lee, M., Katz, H.E., Erben, C., Gill, D.M., Gopalan, P., Heber, J.D. and McGee, D.J., *Science*, 2002, 298: 1401
- 7 Shi, Y., Zhang, C., Zhang, H., Bechtel, J.H., Dalton, L.R., Robinson, B.H., Steier, W.H. and Dalton, L.R., *Science*, 2000, 288: 119
- 8 McLaughlin, C.V., Hayden, M., Polishak, B., Huang, S., Luo, J.D., Kim, T.D. and Jen, A.K.Y., *Appl. Phys. Lett.*, 2008, 92: 15507
- 9 Dalton, L.R., Sullivan, P.A. and Bale, D.H., *Chem. Rev.*, 2010, 110: 25
- 10 Luo, J., Zhou, X. and Jen, A.K.Y., *J. Mater. Chem.*, 2009, 19: 7410
- 11 Luo, J., Huang, S., Shi, Z., Polishak, B., Zhou, X. and Jen, A.K.Y., *Chem. Mater.*, 2011, 23: 544
- 12 Robinson, B.H. and Dalton, L.R., *J. Phys. Chem. A*, 2000, 104: 4785
- 13 Robinson, B.H., Dalton, L.R., Harper, H.W., Ren, A., Wang, F., Zhang, C., Todorova, G., Lee, M., Anisfeld, R., Garner, S., Chen, A., Steier, W.H., Houbrecht, S., Persoons, A., Ledoux, I., Zyss, J. and Jen, A.K.Y., *Chem. Phys.*, 1999, 245: 35
- 14 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. and Jen, A.K.Y., *J. Mater. Chem.*, 1999, 9: 1905
- 15 Cho, M.J., Choe, D.H., Sullivan, P.A., Akelaitis, A.J.P. and Dalton, L.R., *Prog. Polym. Sci.*, 2008, 33: 1013
- 16 Pereverzev, Y.V., Gunnerson, K.N., Prezhd, O.V., Sullivan, P.A., Liao, Y., Olbricht, B.C., Akelaitis, A.J.P., Jen, A.K.Y. and Dalton, L.R., *J. Phys. Chem. C*, 2008, 112: 4355
- 17 Ma, H., Liu, S., Luo, J., Suresh, S., Liu, L., Kang, S.H., Haller, M., Sassa, T., Dalton, L.R. and Jen, A.K.Y., *Adv. Funct. Mater.*, 2002, 12: 565
- 18 Shi, W., Luo, J., Huang, S., Zhou, X., Kim, T.D., Cheng, Y.J., Polishak, B.M., Younkin, T.R., Block, B.A. and Jen, A.K.Y., *Chem. Mater.*, 2008, 20: 6372
- 19 Sunder, A., Heinemann, J. and Frey, H., *Chem. Eur. J.*, 2000, 6: 2499
- 20 Häußler, M. and Tang, B., *Adv. Polym. Sci.*, 2007, 209: 1
- 21 Scholl, M., Kadlecova, Z. and Klok, H.A., *Prog. Polym. Sci.*, 2009, 34: 24
- 22 Zhi, L.J., Wu, J.S., Li, J.X., Stepputat, M., Kolb, U. and Müllen, K., *Adv. Mater.*, 2005, 17: 1492
- 23 Gao, C. and Yan, D., *Prog. Polym. Sci.*, 2004, 29: 183
- 24 Hawker, C.J., *Adv. Polym. Sci.*, 1999, 147: 113
- 25 Tomalia, D.A., *Prog. Polym. Sci.*, 2005, 30: 294
- 26 Voit, B.I. and Lederer, A., *Chem. Rev.*, 2009, 109: 5924
- 27 Li, Z., Qin, Z., Lam, J.W.Y., Dong, Y., Dong, Y., Ye, C., Williams, I. and Tang, B., *Macromolecules*, 2006, 39: 1436
- 28 Bai, Y., Song, N., Gao, J., Sun, X., Wang, X., Yu, G. and Wang, Z., *J. Am. Soc. Chem.*, 2005, 127: 2060
- 29 Zhu, Z., Li, Z., Tan, Y., Li, Z., Li, Q., Zeng, Z., Ye, C. and Qin, J., *Polymer*, 2006, 47: 7881
- 30 Li, Z., Wu, W., Ye, C., Qin, J. and Li, Z., *Macromol. Chem. Phys.*, 2010, 211: 916
- 31 Li, Z., Wu, W., Ye, C., Qin, J. and Li, Z., *Polym. Chem.*, 2010, 1: 78
- 32 Li, Z., Wu, W., Ye, C., Qin, J. and Li, Z., *Polymer*, 2012, 53: 153
- 33 Li, Z., Li, Z., Di, C., Zhu, Z., Li, Q., Zeng, Q., Zhang, K., Liu, Y., Ye, C. and Qin, J., *Macromolecules*, 2006, 39: 6951
- 34 Zeng, Q., Li, Z., Li, Z., Ye, C., Qin, J. and Tang, B., *Macromolecules*, 2007, 40: 5634
- 35 Li, Q., Li, Z., Zeng, F., Gong, W., Li, Z., Zhu, Z., Zeng, Q., Yu, S., Ye, C. and Qin, J., *J. Phys. Chem. B*, 2007, 111: 508
- 36 Li, Z., Li, P., Dong, S., Zhu, Z., Li, Q., Zeng, Q., Li, Z., Ye, C. and Qin, J., *Polymer*, 2007, 48: 3650
- 37 Li, Z., Dong, S., Yu, G., Li, Z., Liu, Y., Ye, C. and Qin, J., *Polymer*, 2007, 48: 5520
- 38 Li, Z., Dong, S., Li, P., Li, Z., Ye, C. and Qin, J., *J. Polym. Sci., Part A: Polym. Chem.*, 2008, 46: 2983
- 39 Li, Z., Li, Q. and Qin, J., *Polym. Chem.*, 2011, 2: 2723
- 40 Li, Z., Hu, P., Yu, G., Zhang, W., Jiang, Z., Liu, Y., Ye, C., Qin, J. and Li, Z., *Phys. Chem. Chem. Phys.*, 2009, 11: 1220
- 41 Li, Q., Yu, G., Huang, J., Liu, H., Li, Z., Ye, C., Liu, Y. and Qin, J., *Macromol. Rapid Commun.*, 2008, 29: 798
- 42 Li, Z., Wu, W., Yu, G., Liu, Y., Ye, C., Qin, J. and Li, Z., *ACS Appl. Mater. Inter.*, 2009, 1: 856
- 43 Campbell, V.E., In, I., McGee, D.J., Woodward, N., Caruso, A. and Gopalan, P., *Macromolecules*, 2006, 39: 597

- 44 Wu, W., Wang, C., Zhong, C., Ye, C., Qiu, G., Qin, J. and Li, Z., *Polym. Chem.*, 2013, 4: 378
- 45 Wu, W., Ye, C., Yu, G., Liu, Y., Qin, J. and Li, Z., *Chem. Eur. J.*, 2012, 18: 4426
- 46 Wu, W., Li, C., Yu, G., Liu, Y., Ye, C., Qin, J. and Li, Z., *Chem. Eur. J.*, 2012, 18: 11019
- 47 Wu, W., Huang, L., Xiao, L., Huang, Q., Tang, R., Ye, C., Qin, J. and Li, Z., *RSC Adv.*, 2012, 2: 6520
- 48 Rostovtsev, V.V., Green, L.G., Fokin, V.V. and Sharples, K.B., *Angew. Chem. Int. Ed.*, 2002, 41: 2596
- 49 Binder, W.H. and Sachsenhofer, R., *Macromol. Rapid Commun.*, 2007, 28: 15
- 50 Lutz, J.F., *Angew. Chem. Int. Ed.*, 2007, 46: 1018
- 51 Li, Z., Di, C., Zhu, Z., Yu, G., Li, Z., Zeng, Q., Li, Q., Liu, Y. and Qin, J., *Polymer*, 2006, 47: 7889
- 52 Muchtar, Z., Schappacher, M. and Deffieux, A., *Macromolecules*, 2001, 34: 7595
- 53 Weimer, M.W., Fréchet, J.M.J. and Gitsov, I. J., *Polym. Sci., Part A: Polym. Chem.*, 1998, 36: 955
- 54 Kim, Y. and Webster, O.W., *Macromolecules*, 1992, 25: 5561