New Hyperbranched Second-Order Nonlinear Optical Poly(arylene-ethynylene)s Containing Pentafluoroaromatic Rings as Isolation Group: Facile Synthesis and Enhanced Optical Nonlinearity Through Ar-Ar^F Self-Assembly Effect

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ABSTRACT: In this article, a facile route was designed to prepare four new hyperbranched poly(arylene-ethynylene)s containing azo-chromophore moieties through one-pot "A₂+B₃" approach via simple Sonogashira coupling reaction. The polymers were all soluble in organic solvents and demonstrated good nonlinear optical (NLO) properties, because of the three-dimensional spatial isolation effect of these hyperbranched

INTRODUCTION During the last two decades, dendritic macromolecules have attracted much interest due to their unique chemical and physical properties such as good solubility and low viscosity, derived from their branching topological structures.¹⁻³⁰ Hyperbranched polymers are of special interest for their easy synthetic accessibility, typically by one pot syntheses. This allows for their production in large quantities and their application on an industrial scale, $^{1,16-23}$ in contrast to dendrimers, which are always prepared tediously and expensively as a result of repetitive protection, deprotection, and purification steps.^{24–30} Usually, the synthetic routes of hyperbranched polymers are either the polymerization of AB_n -type monomers (when *n* is 2 or greater),³¹ or through copolymerization of A_2 and B_n (when *n* is not less than 3). $^{32-35}$ As A₂- and B₃-type monomers were much more stable and easier to be obtained than the AB_n -type ones, there were more and more researches of the hyperbranched polymers derived from " A_2+B_3 " polymerization procedures, and some monomers have been already prepared on an industrial scale. At present, this type of hyperbranched polymers have been intensively explored in many research fields, such as organic light-emitting devices, liquid crystal devices, twophoton absorption materials, supermolecular assembly, drug release, chemsensors, nanoscale catalysis, and so on,36-40

polymers. Due to the different B₃-type comonomer, the self-assembly effect of pentafluoroaromatic in the interior of these polymers were different, leading to the different trends of the NLO activities. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: functionalization of polymers; hyperbranched; NLO

because of the efforts of scientists. Based on the unique properties of hyperbranched polymers, from 2006, our group have been prepared a series of new hyperbranched polymers as nonlinear optical (NLO) polymeric materials (one kind of material with the promise of performance and cost improvements related to telecommunications, computing, embedded network sensing, THz wave generation and detection, and many other applications).⁴¹⁻⁴⁷ The three-dimensional (3D) spatial separation of the chromophore moieties in the hyperbranched polymers endows the polymers with favorable site isolation effect, which could minimize the strong intermolecular electrostatic interactions among chromophore moieties with high dipole moment, thus enhance the macroscopic optical nonlinearities of polymers, according to our previous work and the literatures.⁴¹⁻⁵¹

On the other hand, different from normal aromatic rings, pentafluoroaromatic rings are electropositive, and this activity could lead to the reversible self-assembly of these two type of aromatic rings, the pentafluoroaromatic rings and the normal benzene ones (Chart 1).⁵² In 2007, by using aromatic/pentafluoroaromatic dendron-substituted NLO chromophores through the presence of these complementary Ar-Ar^F interactions, Jen and coworkers⁵³ developed a new class of molecular glasses (Supporting Information Chart S1),

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CHART 1 Different interactions between different aromatic rings.

which exhibited the improved poling efficiency and much enhanced macroscopic NLO effects (Supporting Information Chart S2). Two years later, they observed the same phenomenon again in another series of dendritic NLO chromophores containing pentafluoroaromatic as the dendron.54 Inspired by their wonderful results, also considering that the properties of the hyperbranched polymers were partially dominated by the nature of their large amounts of end groups in the periphery, we designed and synthesized a series of azo chromophore-containing AB₂-type hyperbranched polytriazoles (PS1-PS4, Supporting Information Chart S3) bearing pentafluoroaromatic rings in different part of these hyperbranched polymers.⁴⁵ The pentafluorophenyl groups in the periphery produced higher d_{33} values than the normal phenyl ones in the periphery, whereas the pentafluoroaromatic rings in the interior architecture produced slightly lower d_{33} values, possibly due to the lower loading density of the effective chromophore moieties (Supporting Information Table S1). Thus, it is necessary to design a new series of NLO hyperbranched polymers to investigate whether the pentafluoroaromatic rings in the interior architecture could have a self-assembly effect on normal phenyl rings, and whether this effect could lead to higher d_{33} values as dendron-substituted NLO chromophores reported before. From this standpoint, four new nitro-based azo chromophore containing NLO hyperbranched polymers P1-P4 (Scheme 1) were designed and prepared successfully through a one-pot " A_2+B_3 " approach via Sonogashira coupling reaction. In **P2** and P4, the isolation groups were pentafluoroaromatic rings,

instead of normal phenyl rings in P1 and P3. And this change could only alter the loading density of the effective chromophore moieties at a very limited degree, which would perhaps facilitate the comparison of their properties on the same level. Also, due to the different comonomers, the selfassembly behavior in P2 and P4 was different, leading to their different NLO activities. In comparison with P1 containing normal phenyl rings as isolation groups or its corresponding chromophore C2, there were many evidences, such as much higher glass transition temperature and different NMR spectra, to confirm the presence of these self-assembly in P2. And these interactions resulted in much higher NLO coefficient (up to 78.9 pm V^{-1}), twice higher than that of **P1** (38.1 pm V^{-1}). However, the self-assembly effect did not exist in P4, possibly caused by its too small comonomer unit, which could not supply enough normal phenyl rings for the self-assembly effect. Herein, we would like to present the syntheses, characterization, and properties of these new hyperbranched polymers in detail.

EXPERIMENTAL

Materials and Instrumentation

Tetrahydrofuran (THF) was dried over and distilled from K-Na alloy under an atmosphere of dry nitrogen. Triethylamine (Et_3N) was distilled under normal pressure and kept over potassium hydroxide. Dichloromethane (CH_2Cl_2 , DCM) was dried over from CaH_2 and distilled under normal pressure before use. *N*, *N*-Di(4-pentynyl)benzenamine (**S1**) and



SCHEME 1 The synthesis of NLO hyperbranched polymers.

diazonium fluoroborate **S2** have been prepared in our previous work.⁵⁵ Aryl halides **S4** and **S5** were synthesized through the same way in our previous work.⁴¹ Pentafluorobenzoic acid was purchased from Alfa-Aesar. All other reagents were used as received.

¹H NMR and ¹³C NMR spectra were measured on a Varian Mercury300 or Bruker ARX400 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer-2 spectrometer in the region of 3000-400 cm^{-1} . Ultraviolet-visible (UV-vis) spectra were obtained using a Shimadzu UV-2550 spectrometer. Elemental analyses (EA) were performed by a CARLOERBA-1106 microelemental analyzer. 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⁻¹. Thermal analysis was performed on NETZSCH STA449C thermal analyzer at a heating rate of 10 $^{\circ}$ C min⁻¹ in nitrogen at a flow rate of 50 cm³ min⁻¹ for thermogravimetric analysis (TGA) and the thermal transitions of the polymers. The thickness of the films was measured with an Ambios Technology XP-2 profilometer.

Synthesis of Chromophore S3

N, *N*-Di(4-pentynyl)benzenamine (**S1**) (901.3 mg, 4.0 mmol) and diazonium salt **S2** (1.19 g, 4.0 mmol) were dissolved in 8 mL *N*,*N*-dimethylformamide (DMF)/THF (1/1, v/v) at 0 °C. The reaction mixture was stirred for 12 h at 0 °C, and then treated with H₂O and extracted with CH₂Cl₂, washed with brine. The organic layer was dried over anhydrous sodium sulfate. After removal of the organic solvent, the crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (2/1, v/v) as eluent to afford deep red solid (1.1 g, 63.3%). IR (KBr), ν (cm⁻¹):

3296 (C=C-H), 1517, 1337 (-NO₂). ¹H NMR (400 MHz, CDCl₃, 298 K), δ (TMS, ppm): 1.88 (m, 4H, -CH₂--), 2.05 (s, 2H, -C=C-H), 2.30 (m, 4H, -CH₂--), 3.59 (t, J = 6.0 Hz, 4H, -NCH₂--), 4.00 (t, J = 4.0 Hz, 2H, -OCH₂--), 4.37 (t, J = 4.0 Hz, 2H, -OCH₂--), 4.37 (t, J = 8.0 Hz, 2H, -OCH₂--), 6.80 (d, J = 8.0 Hz, 2H, ArH), 7.72 (d, J = 8.0 Hz, 1H, ArH), 7.86 (d, J = 8.0 Hz, 2H, ArH), 7.95 (m, 2H, ArH). ¹³C NMR (75 MHz, CDCl₃, 298 K), δ (TMS, ppm): 16.2, 26.0, 50.2, 61.2, 69.8, 73.0, 83.3, 111.6, 111.7, 118.3, 126.7, 144.2, 147.9, 148.2, 151.6, 154.9. C₂₄H₂₆N₄O₄ (EA) (%, found/calcd): C, 66.29/66.34; H, 6.36/6.03; N, 12.51/ 12.89. UV-vis (THF, 1 × 10⁻⁵ mmol mL⁻¹): λ_{max} (nm): 493.

General Procedure for the Synthesis of Chromophore C1 and C2

Chromophore **S3** (1.00 equiv.), carboxyl-containing compound (1.50 equiv.), 1-(3-Dimethylaminopropyl)-3-ethylcarbodi-imide hydrochloride (EDC; 2.00 equiv.), and 4-(*N*, *N*dimethyl)aminopyridine (DMAP; 0.20 equiv.) were dissolved in dry CH_2Cl_2 (0.1 mmol mL⁻¹ of chromophore **S3**) and stirred at room temperature for 3 h, and then treated with saturated solution of citric acid and extracted with CH_2Cl_2 , washed with saturated solution of citric acid and brine. After removal of all the solvent, the crude product was purified by column chromatography on silica gel.

Chromophore C1

Reactants: chromophore **S3** (499.7 mg, 1.15 mmol), benzoic acid (211.3 mg, 1.73 mmol). The crude product was purified by column chromatography on silica gel using ethyl acetate/ chloroform (1/20, v/v) as eluent to afford deep red solid (614.3 mg, 99.2%). IR (KBr), v (cm⁻¹): 3267 (C=C-H), 1711 (C=O), 1519, 1335 (-NO₂). ¹H NMR (400 MHz, CDCl₃, 298 K), δ (TMS, ppm): 1.87 (m, 4H, -CH₂--), 2.06 (s, 2H, -C=C-H), 2.30 (m, 4H, -CH₂--), 3.58 (t, J = 8.0 Hz, 4H, -NCH₂--), 4.62 (t, J = 4.0 Hz, 2H, -OCH₂--), 4.80 (t, J = 4.0 Hz, 2H, -OCH₂--), 4.80 (t, J = 8.0 Hz, 2H, ArH), 7.55 (t, J = 8.0 Hz, 1H, ArH), 7.69 (d, J = 8.0 Hz, 1H, ArH), 7.86 (d, J = 8.0 Hz, 1H, ArH), 7.92 (m,



1H, ArH), 8.05 (m, 3H, ArH), 8.17 (d, J = 8.0 Hz, 1H, ArH). ¹³C NMR (75 MHz, CDCl₃, 298 K), δ (TMS, ppm): 49.5, 61.7, 64.1, 67.9, 101.0, 110.2, 111.6, 117.3, 126.0, 128.7, 130.7, 137.6, 144.8, 147.0, 148.0, 150.7, 154.5, 165.7. C₃₁H₃₀N₄O₅ (EA) (%, found/calcd): C, 68.77/69.13; H, 6.06/5.61; N, 10.06/10.40. UV-vis (THF, 1 × 10⁻⁵ mmol mL⁻¹): λ_{max} (nm): 489.

Chromophore C2

Chromophore S3 (499.7 mg, 1.15 mmol), pentafluorobenzoic acid (365.8 mg, 1.73 mmol). The crude product was purified by column chromatography on silica gel using ethyl acetate/ chloroform (1/20, v/v) as eluent to afford deep red solid (686.2 mg, 94.9%). IR (KBr), v (cm⁻¹): 3299 (C≡C−H), 1743 (C=O), 1516, 1336 (-NO₂). ¹H NMR (400 MHz, CDCl₃, 298 K), δ (TMS, ppm): 1.87 (m, 4H, -CH₂-), 2.05 (s, 2H, $-C \equiv C - H$), 2.30 (m, 4H, $-CH_2$ -), 3.58 (t, J = 8.0 Hz, 4H, $-NCH_2$, 4.56 (t, J = 4.0 Hz, 2H, $-OCH_2$), 4.88 (t, J = 4.0Hz, 2H, $-COOCH_2$ -), 6.76 (d, J = 8.0 Hz, 2H, ArH), 7.69 (d, J= 8.0 Hz, 1H, ArH), 7.83 (d, J = 8.0 Hz, 2H, ArH), 7.94 (m, 2H, ArH). ¹³C NMR (75 MHz, CDCl₃, 298 K), δ (TMS, ppm): 15.9, 25.7, 49.9, 64.2, 67.9, 69.4, 83.0, 110.2, 111.2, 117.5, 126.3, 144.1, 147.5, 147.8, 151.1, 154.4, 158.9. C₃₁H₂₅N₄O₅F₅ (EA) (%, found/calcd): C, 59.24/59.66; H, 3.95/4.01; N, 8.91/ 8.91. UV-vis (THF, 1×10^{-5} mmol mL⁻¹): λ_{max} (nm): 489.

General Procedure for the Synthesis of P1-P4

A mixture of chromophore **C1** or **C2** (1.50 equiv.), aryl halides **S4** or **S5** (1.00 equiv.), copper iodide (Cul) (5 mol %), triphenylphosphine (PPh₃) (5 mol %), tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄) (3 mol %), was carefully degassed and charged with argon. THF (monomer **C1** or **C2** concentration was ca. 0.025 mmol mL^{-1})/Et₃N (3/1 by volume) was then added. The reaction was stirred for an appropriate time at an appropriate temperature. The mixture was passed through a cotton filter and dropped into a lot of methanol. The precipitate was collected, further purified by several precipitations of its THF solution into acetone, and dried in a vacuum at 40 °C to a constant weight.

P1

Chromophore **C1** (80.8 mg, 0.15 mmol), **S4** (48.2 mg, 0.10 mmol), reaction temperature: 60 °C, reaction time: 36 h. **P1** was obtained as a deep red powder (91.0 mg, 86.8%). $M_w = 7300$, $M_w/M_n = 1.70$ (GPC, polystyrene calibration). IR (KBr), v (cm⁻¹): 1515, 1336 (—NO₂). ¹H NMR (300 MHz, CDCl₃ 298 K), δ (TMS, ppm): 1.7–2.1 (—CH₂—), 2.1–2.6 (—CH₂—), 3.1–3.8 (—NCH₂—), 4.3–4.8 (—OCH₂— and —COOCH₂—), 6.4–7.0 (ArH), 7.0–8.1 (ArH). ¹³C NMR (75 MHz, CDCl₃ 298 K), δ (TMS, ppm): 17.06, 26.03, 50.33, 63.31, 68.79, 110.83, 111.69, 113.60, 117.63, 126.14, 126.62, 128.59, 129.96, 132.72, 133.33, 134.52, 147.62, 155.03, 166.62. UV-vis (THF, 0.02 mg mL⁻¹): λ_{max} (nm): 490.

P2

Chromophore **C2** (94.28 mg, 0.15 mmol), **S4** (48.2 mg, 0.10 mmol), reaction temperature: 60 °C, reaction time: 40 h. **P2** was obtained as a deep red powder (84.1 mg, 71.1%). $M_w = 6700$, $M_w/M_n = 1.66$ (GPC, polystyrene calibration). IR (KBr), v (cm⁻¹): 1718 (C=O), 1515, 1335 (-NO₂). ¹H NMR

(300 MHz, CDCl₃ 298 K), δ (TMS, ppm): 1.7–2.1 (–CH₂–), 2.2–2.6 (–CH₂–), 3.1–3.7 (–NCH₂–), 4.3–4.6 (–OCH₂–), 4.6–4.8 (–COOCH₂–), 6.4–7.0 (ArH), 7.0–8.0 (ArH). ¹³C NMR (75 MHz, CDCl₃, 298 K), δ (TMS, ppm): 17.08, 26.04, 25.34, 50.42, 64.42, 68.19, 110.47, 111.59, 117.85, 123.48, 125.87, 126.19, 126.57, 128.69, 128.84, 132.26, 132.40, 132.75, 144.18, 144.49, 146.21, 147.66, 148.17, 154.69, 159.19. UVvis (THF, 0.02 mg mL⁻¹): λ_{max} (nm): 492.

P3

Chromophore **C1** (80.8 mg, 0.15 mmol), **S5** (52.8 mg, 0.10 mmol), reaction temperature: 30 °C, reaction time: 40 h. **P3** was obtained as a deep red powder (85.9 mg, 90.3%). $M_w =$ 9800, $M_w/M_n =$ 1.53 (GPC, polystyrene calibration). IR (KBr), v (cm⁻¹): 1516, 1337 (-NO₂). ¹H NMR (300 MHz, CDCl₃ 298 K), δ (TMS, ppm): 0.6–1.2 (-CH₃), 1.2–2.1 (-CH₂--), 2.2–2.7 (-CH₂--), 3.2–3.8 (-NCH₂--), 3.8–4.2 (-OCH₂--) 4.3–4.8 (-OCH₂-- and -COOCH₂--), 6.8–7.0 (ArH), 7.2–8.2 (ArH). ¹³C NMR (75 MHz, CDCl₃, 298 K), δ (TMS, ppm): 14.00, 16.94, 19.18, 26.09, 29.66, 32.04, 50.20, 63.12, 68.64, 90.38, 110.78, 111.44, 117.38, 122.88, 126.39, 128.33, 129.70, 133.09, 142.45, 144.34, 147.91, 154.82, 160.55, 166.36. UV-vis (THF, 0.02 mg mL⁻¹): λ_{max} (nm): 492.



Chromophore **C2** (94.28 mg, 0.15 mmol), **S5** (52.8 mg, 0.10 mmol), reaction temperature: 30 °C, reaction time: 48 h. **P4** was obtained as a deep red powder (94.1 mg, 87.0%). $M_w = 8800$, $M_w/M_n = 1.53$ (GPC, polystyrene calibration). IR (KBr), v (cm⁻¹): 1724 (C=O), 1517, 1334 (-NO₂). ¹H NMR (300 MHz, CDCl₃ 298 K), δ (TMS, ppm): 0.8–1.1 (-CH₃), 1.2–1.3 (-CH₂--), 1.5–2.1 (-CH₂--), 2.2–2.7 (-CH₂--), 3.3–3.8 (-NCH₂--), 3.8–4.1 (-OCH₂--), 4.4–4.6 (-OCH₂--) 4.7–5.0 (-COOCH₂--), 6.7–6.9 (ArH), 7.4–8.1 (ArH). ¹³C NMR (75 MHz, CDCl₃ 298 K), δ (TMS, ppm): 13.97, 16.91, 19.15, 23.34, 25.97, 32.01, 32.23, 50.18, 64.19, 66.86, 68.01, 90.32, 110.32, 111.31, 117.55, 122.83, 126.30, 128.43, 128.51, 131.99, 132.05, 132.61, 136.65, 138.33, 142.43, 144.23, 144.67, 146.34, 147.86, 154.42, 157.88, 158.84. UV-vis (THF, 0.02 mg mL⁻¹): λ_{max} (nm): 492.

Preparation of Polymer Thin Films

The polymers were dissolved in THF (concentration ~ 3 wt %), and the solutions were filtered through syringe filters. Polymer films were spin coated onto indium-tin-oxide-coated glass substrates, which were cleaned by DMF, acetone, distilled water, and THF sequentially in an ultrasonic bath before use. 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 3); voltage, 7.5 kV at the needle point; gap distance, 0.8 cm. The SHG measurements were performed

TABLE 1 Characterization Data of Polymers

No.	7ª (°C)	t ^b (h)	Yield (%)	<i>M</i> w ^c	$M_{ m w}/M_{ m n}^{ m c}$	7g ^d (°C)	T _d ^e (°C)
P1	60	36	86.8	7300	1.70	116	271
P2	60	40	71.1	6700	1.66	164	222
P3	30	40	90.3	9800	1.53	111	239
P4	30	48	87.0	8800	1.53	80	205

^a Reaction temperature.

^b Reaction time.

^c Determined by GPC in THF on the basis of a polystyrene calibration.

 $^{\rm d}$ Glass transition temperature ($T_{\rm g})$ of polymers detected by the DSC analyses under argon at a heating rate of 10 $^\circ {\rm C}$ min $^{-1}.$

^e The 5% weight loss temperature of polymers detected by the TGA analyses under nitrogen at a heating rate of 10°C min⁻¹.

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 overall pathway of the monomer synthesis was presented in Scheme 1. Usually, in the azo-coupling reaction, diazonium hydrochloride was used as azo reagents, due to its high reaction activity.^{41–47} However, for the synthesis of chromophore **S3**, there was no product yielded using this way, no matter we changed the different reaction conditions just like the concentration and pH values. Thus, fluoborate salt was used instead of the normal hydrochloride salt as the azo reagent. Even so, the yield (63.3%) was a little lower than normal azo-coupling reactions between aniline and *p*nitroaniline. Then, the monomers (chromophores **C1** and **C2**) were prepared by the esterification of chromophores **S3** with benzoic acid or pentafluorobenzoic acid under mild conditions, in which phenyl or pentafluorophenyl groups act as isolation spacers.

As shown in Scheme 1, the target hyperbranched poly(arylene-ethynylene)s **P1-P4** could be prepared successfully via a typical Sonogashira crosscoupling reaction between different chromophores and aryl halides, catalyzed by $Pd(PPh_3)_4$, PPh_3 , and CuI, similar to our previous work.^{41,55} The reactivity of different aryl halides was much different during the Sonogashira crosscoupling procedure: aryl iodide could react with terminal alkyne under room temperature, while aryl bromide could only react at higher temperature such as 5060 °C. Herein, to control the polymerization procedure under mild conditions, the reaction temperature was fixed at 60 (P1 and P2) or 30 °C (P3 and P4). On the other hand, the copolymerization of A2 and B3 monomers might lead to the formation of gelation, and the reaction time must be also controlled carefully to avoid the possible formation of gelation, with the aim to get soluble hyperbranched polymers.⁴¹ Thus, the reaction should be terminated before the formation of gelation, and the reaction time for different polymers was also different (36 h, 40 h, 40 h, and 48 h, respectively), due to their different comonomer, as shown in experimental section and Table 1. The obtained hyperbranched polymers P1-P4 were readily soluble in common polar organic solvents, such as C H₂Cl₂, CHCl₃, THF, DMF, and DMSO, and their solutions could be easily spin-coated into thin solid films. Thus, it was convenient to test their NLO and other properties based on the solutions and thin films.

Characterizations

The prepared chromophores and polymers were characterized by spectroscopic methods, and all gave satisfactory spectral data (see Experimental section and Supporting Information for detailed analysis data). All the chromophores and polymers are new compounds. Supporting Information Figures S1 and S2 showed the FTIR spectra of the polymers P1, P3 and P2, P4 and their corresponding chromophores, respectively, in which the absorption bands associated with the nitro groups and carbonyl groups are at about 1338, 1517, and 1720 cm^{-1} , respectively, showing that the chromophore and isolation groups were stable during the Sonogashira polymerizations. At the same time, an absorption band derived from the \equiv C–H stretching vibrations appeared at about 3277 cm^{-1} in the FTIR spectra of chromophores **C1** and C2 but disappeared in the spectra of their corresponding polymers P1-P4, indicating the polymerizations were successful.

In the ¹H NMR and ¹³C NMR spectra (see Supporting Information) of the chromophores and polymers, no unexpected resonance peaks were observed, and the chemical shifts were consistent with the proposed polymer structure (Schemes 1 and 2). To further confirm the structure of the chromophore and polymers containing pentafluorophenyl groups, their ¹⁹F NMR spectra (see Supporting Information) were also tested. The ¹H NMR spectra of hyperbranched polymers **P1–P2** and their corresponding chromophores **C1– C2**, which were conducted in the solvent of chloroform-*d* were shown in Figure 1. Except the peaks associated to the



SCHEME 2 The synthesis of chromophores.





FIGURE 1 ¹H NMR spectra of hyperbranched polymers P1–P2 and their corresponding chromophores C1–C2 in chloroform-*d*.

protons of isolation groups (phenyl or pentafluorophenyl), there was another difference between the ¹H NMR spectra of **C1** and **C2**: the chemical shift of the group of $-COOCH_2$ in C1 was 4.80, while 4.88 in C2. This should be ascribed to the different electron behaviors of phenyl or pentafluorophenyl groups. Due to the highest electronegativity of fluorine atom, the pentafluoroaromatic rings were electropositive, making the electron withdrawing activity of pentafluorobenzoic groups much stronger than that of benzoic ones. Thus, the chemical shifts of protons next to them were different. After polymerizations, all the peaks showed an inclination of signal broadening obviously, and the disappearance of the single peaks associated with the protons of C≡CH around 2.05 ppm (Fig. 1 was an example) confirmed that the polymerizations were successful again. However, the chemical shifts of protons next to the pentafluorobenzoic $(-COOCH_2-)$ in the ¹H NMR spectrum of **P2** became

smaller, in comparison with its corresponding chromophore C2 (Fig. 1), disclosing that the electron withdrawing activity of pentafluorobenzoic groups became weaker, and the electron density distribution of pentafluoroaromatic rings became higher. This phenomenon should be caused by the self-assembly effect between pentafluoroaromatic rings and the aromatic ones in the triphenylamine (TPA) comonomer units. But this exciting phenomenon was not observed in the ¹H NMR spectrum of **P4**, no matter **P4** had the similar chemical structure to P2. This was understandable. As shown in Figure 2, the comonomer unit for P4 was 2-butoxy-1,3,5triiodobenzene (S5), in which there was only one phenyl rings, different from the three ones of TPA unit in P2. After polymerization, in P4, there were three chromophore moieties (C2) containing pentafluoroaromatic rings around that phenyl ring. Thus, it might not be enough (one normal benzene ring vs. three pentafluoroaromatic rings) to have the effect of self-assembly with pentafluoroaromatic rings. Moreover, the large steric effect of P4, caused by the so small comonomer unit, could also limit the self-assembly between the two types of aromatic rings. On the contrary, there might be some interactions between the more electropositive pentafluoroaromatic rings and other aromatic ones, which would perhaps destroy the comparative perfect 3D structure of hyperbranched polymers to some extent. We would discuss this point later.

The molecular weights of polymers were determined by GPC with THF as an eluent and polystyrene standards as calibration standards. As shown in Table 1 and the Experimental section, P1 and P2 showed little lower molecular weights than P3 and P4, this should be caused by the lower reaction activity of aryl bromide. Interestingly, P2 and P4 also exhibited a little lower molecular weights than their corresponding polymers P1 and P3, indicating that the introduction of pentafluoroaromatic rings would make the activity of Sonogashira reaction a little lower. Anyhow, the molecular weights of these four hyperbranched polymers were on the same level, around 8000 g mmol $^{-1}$. It should be pointed out that the GPC analysis using linear polystyrenes as calibration standards often underestimates the molecular weights of hyperbranched polymers, with difference as big as ${\sim}40$ times being reported before.^{56–58} The actual or true molecular weights of these poly(arylene-ethynylene)s thus could be much higher than the values given in Table 1.

Their TGA thermograms were shown in Figure 3, and the 5% weight loss temperature (T_d) of polymers was listed in Table 1. All the polymers were thermally stable with the T_d values higher than 200 °C. **P2** and **P4** exhibited worse thermal stability than **P1** and **P3**, indicating that the pentafluorophenyl group was not so stable. But this was already enough for NLO materials, because the temperature for its real application was generally lower than 200 °C. And **P1** and **P2** demonstrated higher T_d s than **P3** and **P4**, as the comonomer unit of **P3** and **P4** was so small and the large steric effect might decrease the ability of thermolytically resistant. The glass transition temperatures (T_g) of the polymers were also investigated by using a differential scanning calorimeter,

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FIGURE 2 Different self-assembly behaviors of Ar-Ar^F in P2 and P4.

with the results summarized in Table 1. **P1** and **P3** exhibited similar T_g values of 116 and 111 °C, respectively, due to their similar chemical structure. However, after the introduction of pentafluoroaromatic rings, different trend was observed. Because of the intensive self-assembly effect, the T_g value of **P2** increased a large degree (up to 164 °C) in comparison with that of **P1**, while **P4** had lower T_g value (80 °C) than **P3**. This was reasonable. Some interactions between the more electropositive pentafluoroaromatic rings and other aromatic ones could destroy the comparative perfect 3D structure of hyperbranched polymers as aforementioned. The increasing T_g value of **P2** was another evidence to confirm the presence of self-assembly effect in **P2**.

The UV-vis absorption spectra of the chromophores and polymers in different solvents were demonstrated in Figures 4 and S19–S23 (Supporting Information), and the maximum absorption wavelengths (λ_{max}) for the π - π * transition of the azo moieties in them were listed in Table 2. All the polymers exhibit similar λ_{max} values, nearly the same as their corresponding chromophores. These results indicated that the introduction of pentafluoroaromatic rings nearly did not affect the $\mu\beta$ value of chromophore moieties, thus, the comparison of their NLO properties was at the same level.



FIGURE 3 TGA thermograms of **P1–P4**, measured in nitrogen at a heating rate of 10 $^{\circ}$ C min⁻¹.



FIGURE 4 UV-vis spectra of polymers P1-P4 in THF (0.02 mg mL⁻¹).

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TABLE 2 The N	laximum	Absorp	otion of	of Po	lymers	and	their
Corresponding	Chromop	hores	(λ_{\max})	nm)ª	I		

	THF	1,4-Dioxane	Chloroform	Dichloro- methane	DMF	DMSO	Film
P1	490	478	490	496	494	499	505
P2	492	481	491	490	495	505	501
Р3	492	478	488	488	497	503	506
P4	492	479	493	493	500	505	506
C1	489	478	493	494	500	507	
C2	489	479	493	495	500	507	

 a The maximum absorption wavelength of polymers (chromophore molecules) solutions with the concentrations fixed at 0.02 mg mL $^{-1}$ (2.5 \times 10 $^{-5}$ mol mL $^{-1}$).

On the other hand, this phenomenon also indicated that the self-assembly did not occur between pentafluoroaromatic rings and chromophores, and further confirmed that self-assembly behaviors of Ar-ArF in **P2** and **P4** as shown in Figure 2.

NLO Properties

In the excellent work of Jen and coworkers,^{52–54} the complementary Ar-Ar^F interactions could improve the poling efficiency of the dendron-substituted NLO chromophores, leading to the enhanced NLO activities. Herein, would the presence of these self-assembly behaviors lead to the same result in the interior of hyperbranched polymers? If they could, that might be a new way to improve the NLO effects of the hyperbranched polymers. For evaluating the NLO activity of the polymers, their poled thin films were prepared. The most convenient technique to study the second-order NLO activity was to investigate the SHG processes characterized by d_{33} , an SHG coefficient. To check the reproducibility, we repeated the measurements at least three times for each sample. Calculation of the SHG coefficients (d_{33}) for the poled films is based on the following equation:

$$\frac{d_{33,s}}{d_{11,q}} = \frac{\chi_s^{(2)}}{\chi_q^{(2)}} = \sqrt{\frac{I_s}{I_q}} \frac{l_{c,q}}{I_s} F$$

where $d_{11,q}$ is d_{11} of the quartz crystals, which is equal to 0.45 pm V⁻¹. I_s and I_q are the SHG intensities of the sample and the quartz, respectively, $l_{c,q}$ is the coherent length of the quartz, I_s is the thickness of the polymer film, and F is the correction factor of the apparatus and is equal to 1.2 when l_c is much greater than I_s . From the experimental data, the d_{33} values of **P1-P4** were calculated at a fundamental wavelength of 1064 nm (Table 3). Generally, the d_{33} value of the same NLO polymer could be different when measured by different methods or different testing systems at different times. To avoid the aforementioned possible deviations, the NLO properties of all the polymers were tested at the same time.

Due to the similar structure and near the same T_g value, the best poling temperatures of **P1** and **P3** were also near the same. But their NLO coefficients were much different (38.1 and 177.3 pm V⁻¹, respectively), which might be due to

TABLE 3 NLO Activities of Hyperbranched Polymers

No.	T _e ª (∘C)	l _s ^b (μm)	d ₃₃ ℃ (pm V ^{−1})	d _{33(∞)} ^d (pm V ^{−1})	Φ^{e}	N ^f
P1	102	0.32	38.1	2.8	0.07	0.425
P2	145	0.29	78.9	5.8	0.11	0.378
P3	103	0.34	177.3	13.1	0.20	0.506
P4	85	0.29	115.7	8.5	0.10	0.440

^a The best poling temperature.

^b Film thickness.

^c Second harmonic generation (SHG) coefficient.

 $^{\rm d}$ The nonresonant $d_{\rm 33}$ values calculated by using the approximate two-level model.

 $^{\rm e}$ Order parameter $\Phi=1$ – $A_{\rm 1}/A_{\rm 0},$ $A_{\rm 1}$ and $A_{\rm 0}$ are the absorbance of the polymer film after and before corona poling, respectively.

The loading density of the effective chromophore moieties.

different density of the chromophore moieties. According to the one-dimensional rigid orientation gas model:⁵⁹

$$d_{33} = \frac{1}{2} N \beta f^{2\omega} (f^{\omega})^2 \left\langle \cos^3 \theta \right\rangle$$

where *N* is the number density of the chromophore, β is its first hyperpolarizability, *f* is the local field factor, 2ω is the double frequency of the laser, ω is its fundamental frequency, and $\langle \cos^3 \theta \rangle$ is the average orientation factor of the poled film. Obviously, under identical experimental conditions, d_{33} is proportional to the number density of the chromophore. In **P1**, the comonomer unit of TPA, which was much larger than the phenyl one in **P3**, resulted in much lower loading density of the chromophore moieties than that in **P3** (0.425 vs. 0.506). Thus, the much lower d_{33} value of **P1** was understandable. The similar phenomenon has been already observed in our previous work on NLO dendritic macromolecules, including hyperbranched polymers,^{41,45,55} dendrimers,⁶⁰⁻⁶² and dendronized polymers.⁶³ Especially, we have synthesized two other hyperbranched polymers (**PS5**



FIGURE 5 Different poling procedure of different polymers P1 and P2: the curves of the normalized d_{33} values of P1–P2 as a function of the poling temperature.



FIGURE 6 Decay curves of the SHG coefficients of **P1–P4** as a function of the temperature.

and **PS6**, Chart S4 in Supporting Information), with similar structures to **P1** and **P3** but containing no isolation group.⁴¹ Likewise, the d_{33} value of **PS5** was only 55 pm V⁻¹, while 177 pm V⁻¹ for **PS6**.

However, after using pentafluoroaromatic rings as isolation groups instead of phenyl, the trend of NLO activities were totally different. Figure 5 showed the different poling procedure of P1 and P2. It was easily seen that the initial temperatures of them to exhibit NLO activities were almost the same (a little higher than 80 °C). At 102 °C, P1 already achieved the highest value, while the best temperature of P2 was much higher (up to 145 °C). This meant that it was much more difficult than **P1** to pole the thin films of **P2**, possibly caused by the presence of self-assembly effect in the interior of P2. Also, these interactions between aromatic rings and pentafluoroaromatic ones led to higher NLO coefficients, and the d_{33} value of P2 (up to 78.9 pm V^{-1}) was two times higher than that of P1. As mentioned above, due to the so small comonomer units, there should be no self-assembly effect in P4. This point also reflected in the NLO activities: the best poling temperature and d_{33} value were lower than that of **P3**, which just contained normal phenyl as isolation group.

As there might be some resonant enhancement due to the absorption of the chromophore moieties at 532 nm, the NLO properties of polymers should be smaller as shown in Table 3 ($d_{33}(\infty)$), which were calculated by using the approximate two-level model. As all the polymers exhibited nearly the same UV-vis absorption behavior, their $d_{33}(\infty)$ values demonstrated the same phenomena as their d_{33} values.

To further study the alignment behavior of the chromophore moieties in the polymers, the order parameter (Φ) of the polymers (Table 3) was measured and calculated from the change of the UV-vis spectra of their films before and after poling under electric field (Supporting Information Figs. S24 and S25), according to the equation described in Table 2 (footnote e). The tested Φ value of **P2** (0.11) was still higher than that of **P1** (0.07), indicating the good alignment of the

chromophore moieties in the poled film of **P2**, further confirming the advantages of self-assembly effect in NLO hyperbranched polymers. **P4** demonstrated a lower Φ value than **P3**, due to the absence of the self-assembly effect.

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 40 to 140 $^\circ$ C in air at a rate of 4 $^{\circ}$ C min⁻¹. Figure 6 showed the decay of SHG coefficient of P1-P4 as a function of temperature. From the onset temperatures for decays to the temperatures for the NLO activities decreased to 0 pm V^{-1} , **P2** was nearly as large as 40 °C, which were much longer than the other three polymers. That was to say, to destroy the alignment of the chromophore moieties in P2, would need more energy, indicating that the Ar-Ar^F self-assembly effect was still present after poling, and these interactions could increase the stability of NLO hyperbranched polymers. All the NLO behavior (including poling experiment and depoling experiment) of P2 confirmed the alignment formation of NLO materials with the self-assemble effect derived from the Ar-Ar $^{
m F}$ interactions, (Chart S2 in Supporting Information) proposed by Jen and coworkers.53,54

CONCLUSIONS

In summary, four new NLO hyperbranched poly(aryleneethynylene)s containing different type of aromatic rings as isolation groups were prepared successfully via one-pot "A₂+B₃" Sonogashira polymerizations to investigate the Ar-Ar^F self-assembly effect in the NLO hyperbranched polymers. Due to their much different density of the chromophore moieties, P1 and P3, with normal phenyl groups as isolation spacers, demonstrated much different NLO coefficient. Interestingly, after using pentafluoroaromatic rings as isolation groups instead of normal phenyl, the trend of NLO activities were totally different, as a result of their different self-assembly behaviors through the Ar-Ar^F interactions. And because of the Ar-Ar^F self-assembly effect, P2 demonstrated much larger d_{33} values and higher stability than its analog P1. Moreover, the poling and depoling behaviors of P2 confirmed the presence of the self-assemble effect as the result of the Ar-Ar^F interactions. This powerful way to improve the performance of NLO material should be also used in NLO dendrimers, which have better 3D topological structure than hyperbranched polymers and always demonstrate much higher NLO coefficient than hyperbranched polymers, and the work is in progress in our laboratory.

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