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Synthesis and second-order nonlinear optical properties of hyperbranched polymers containing pendant azobenzene chromophores

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Abstract

Two hyperbranched polymers with methyl ester (P1) and epoxy (P2) terminal groups containing pendant azobenzene chromophores were prepared through an "$A_2 + B_3$" approach used for second-order nonlinear optical materials. Their chemical structures were characterized by NMR and GPC analyses. The polymers have good solubility in common organic solvents and film-forming ability. The pure films were fabricated successively without doping into other matrices. The poled films exhibit high second-harmonic generation coefficients (>50 pm/V) due to the three-dimensional spatial isolation effect resulting from their highly branched structures. The optical nonlinearity of the poled P2 film is thermally more stable than that of P1 due to the cross-linking of epoxy groups with carboxylic acid groups in the former during poling. The onset decay temperature of SHG intensity of P2 was determined to be at around 155 °C, which was 20 °C higher than that of P1.

Keywords: Hyperbranched polymer; Nonlinear optical; Cross-linking

1. Introduction

Organic second-order nonlinear optical (NLO) materials have received increasing interests due to their potential for the applications in photonics such as electro-optic (EO) modulators. Compared to traditional inorganic crystals, poled organic polymers offer some advantages such as lower cost, lower dielectric constant and greater EO coefficient that results in higher bandwidth [1–4]. A major effort has been made in order to translate the large molecular first hyperpolarizability into macroscopic EO coefficient [5–7]. However, due to the strong intermolecular electrostatic interactions among high dipole moment chromophores that tend to form aggregates, it is difficult to achieve both large macroscopic nonlinearity and good dipole alignment stability in the same system. Much work has been done to provide a solution to this critical issue. To maintain a stable dipole alignment, either high glass-transition temperature (T_g) polymers with NLO chromophores as side chains or cross-linkable polymers with NLO chromophores, that could be locked in the polymer network, are utilized in common practice [8–11]. Recently, it is theoretically suggested that due to the steric effect the spherical molecular shape can minimize the intermolecular electrostatic interaction, resulting in maximum macroscopic nonlinearity [12,13]. Dendrimers, as a new family of polymers, possess spherical shape and three-dimensional spatial isolation which results in the decrease of chromophore–chromophore electrostatic interaction and thus enhancement of macroscopic optical nonlinearity [14–16]. Similarly to dendrimers, hyperbranched polymers, which are globular macromolecules as well, can minimize the intermolecular electrostatic interactions with their site-isolation effect and optical loss in the NLO process with their large void-containing highly branched structure. Moreover, hyperbranched polymers are much easier to synthesize than dendrimers and can be used to fabricate pure films without doping into other matrices [17,18]. Hyperbranched

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polymers, therefore, are promising candidates for NLO materials with good macroscopic EO activity [19−22].

In this paper, two hyperbranched polymers by containing pendant azobenzene chromophores through solution polycondensation and "$A_2 + B_3$" approach were synthesized. The polymerization was carried out with common chromophore 4-*N*,*N*′-dis(2-hydroxyethyl)amino-4′-nitro-azobenzene (DR19) as an A_2 monomer and 1,3,5-benzenetricarbonyl trichloride (BTC) as a B_3 monomer. The obtained hyperbranched polymers possess good film-forming ability and their pure films were fabricated successively without doping into other matrices such as polycarbonate. To improve the NLO stability, thermally cross-linkable epoxy group was introduced as the terminal functional group of hyperbranched polymer. The epoxy and carboxylic acid end groups of P2 readily underwent thermal cross-linking reaction during poling. The resultant thermosetting network can hamper the thermal depoling process. The second-harmonic generation (SHG) coefficient and the thermal stability of the optical nonlinearity of poled films were investigated.

2. Experimental section

2.1. Materials

1,3,5-Benzenetricarbonyl trichloride (BTC) (99%), *N*-phenyldiethanolamine (95%) and 2,3-epoxy-1-propanol (96%) were purchased from Aldrich and used as received. Triethylamine (TEA) was purified by distillation. DMF was dried over calcium hydride and distilled immediately prior to use. THF, methanol, ethanol and cyclohexanone were dried with Na_2SO_4. All these reagents and solvents were purchased from the First Reagent Co. of Shanghai, China.

2.2. Measurements

The ^{1}H NMR spectra were recorded on a Bruker 300 MHz spectrometer with DMSO-d_6. The FTIR spectra were recorded with a Nicolet MAGNA-IR 750 spectrometer (Nicolet Instrument corp., USA). The KBr-pressed disk method was utilized to prepare the samples. The molecular weight and polydispersity index were determined by a Waters gel permeation chromatography (GPC) system equipped with a refractive index detector, using DMF as an eluent (elution rate: 1 mL/min). The differential scanning calorimetry (DSC) was carried out with a SHIMADZU DSC-60 equipment. All the samples were heated at 10 °C/min from 20 to 200 °C under nitrogen for the first scan, then cooled to 20 °C at 40 °C/min, and immediately heated at 10 °C/min up to 200 °C for the second scan. The thermogravimetric analysis (TGA) was carried out on a SHIMADZU TG-50 instrument using a heating rate of 10 °C/min under nitrogen. The UV−vis spectra were measured on a SHIMADZU UV-2401PC ultraviolet−visible spectrometer in THF and DMF solutions.

2.3. Synthesis of 4-N,N′-bis(2-hydroxyethyl)amino-4′-nitro-azobenzene (DR19)

4-Nitroaniline (2.76 g, 0.02 mol) was firstly dissolved in a solution of concentrated hydrochloric acid (10 mL) in water (100 mL), then immediately added into cold water (100 mL) at 0 °C with an ice bath, and further mixed with the solution of sodium nitrite (1.38 g, 0.02 mol) in water (5 mL) slowly, and stirred for 30 min. The *N*-phenyldiethanolamine (3.62 g, 0.02 mol) solution in ethanol (20 mL) was successively added into the above mixture at 0−5 °C, and stirred in the ice bath for 5 h. The dark red precipitate was formed and filtered, washed with water for several times. The product was further purified by recrystallization from an methanol/ethanol mixture, and dried in vacuum at 40 °C for 24 h (5.94 g, 90% yield), named DR19. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 3.61 (s, 8H, N−CH_2−CH_2−O), 4.88 (s, 2H, CH_2−OH), 6.90 (d, 2H, ArH), 7.81 (d, 2H, ArH), 7.92 (d, 2H, ArH), 8.35 (d, 2H, ArH). IR (KBr) λ (cm^{-1}): 3278 (OH), 1600 (C═C), 1511, 1339 (N═O), 859 (C−C).

2.4. Synthesis of hyperbranched polymer with methyl ester terminal groups

A typical synthetic procedure is as follows: BTC (0.530 g, 2 mmol) was dissolved in 20 mL of freshly distilled DMF in a 150 mL thoroughly dried flask equipped with a magnetic stir bar and an addition funnel. DR19 (0.66 g, 2 mmol) and TEA (0.31 g, 3 mmol) were completely dissolved in 40 mL of freshly distilled DMF, then dropwise added into the reaction flask at 0−5 °C over 1 h, and stirred for 24 h at 25 °C. The reaction mixture was poured into methanol. The precipitated polymer was formed and filtered, redissolved in THF and reprecipitated from methanol. The purified product was collected and dried at 40 °C in vacuum for 24 h (0.542 g, 52.4% yield), named P1. $M_n = 9027$, $M_w/M_n = 1.11$ (GPC, polystyrene calibration). ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 3.49−4.07 (N−CH_2−), 4.07−4.96 (COO−CH_3, COO−CH_2−) 6.62−7.18 (ArH), 7.42−7.94 (ArH), 7.97−8.80 (ArH). IR (KBr) λ (cm^{-1}): 1728 (C═O), 1601 (C═C), 1514, 1340 (N═O), 1139 (C−O−C).

2.5. Synthesis of hyperbranched polymer with epoxy terminal groups

The synthetic process was similar to P1 preparation except that, at the final stage of polymerization of DR19 with BTC, 2,3-epoxy-1-propanol (0.074 g, 1 mmol) was added and stirred for another 12 h. Then distilled water (5 mL) was subsequently added to quench the residual acid chloride, and the reaction mixture was stirred for 30 min. After filtration, the homogeneous solution was poured into methanol. The resulting scarlet powder was collected by filtration, further purified by reprecipitation of its THF solution into methanol and dried at 40 °C in vacuum for 24 h (0.512 g, 49.5% yield), named P2. $M_n = 8304$, $M_w/M_n = 1.15$ (GPC, polystyrene calibration). ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 2.67, 2.92 and

3.25 (−*CH*−*CH*$_2$, protons of epoxy ring), 3.50−4.08 (N−*CH*$_2$−), 4.20−4.76 (COO−*CH*$_2$−) 6.68−7.24 (ArH), 7.46−7.88 (ArH), 7.88−8.62 (ArH), 13.58 (COO*H*). IR (KBr) λ (cm^{-1}): 3430 (OH), 1728 (C=O), 1600 (C=C), 1514, 1340 (N=O), 1139 (C−O−C), 903 (C−O−C, epoxy ring).

2.6. Film fabrication

The hyperbranched polymers were dissolved in cyclohexanone (concentration ~ 2 wt%), and filtered through syringe filters, then spin-coated onto the indium-tin oxide (ITO)-coated glass substrates, which were carefully pre-cleaned by DMF, acetone, distilled water, and THF sequentially in an ultrasonic bath. The films were dried in a vacuum oven at 60 °C for 24 h. The film thickness was measured by an Alpha-step 500 Surface Profiler.

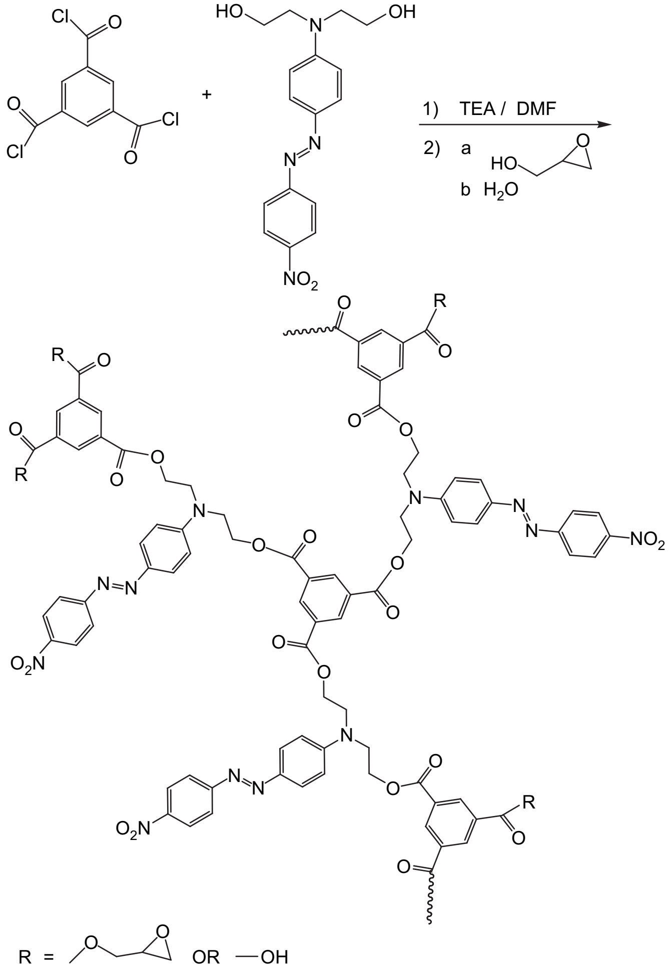
2.7. Poling process and SHG measurement

The poling process for the second-order NLO polymer films was carried out using a corona poling technique. The corona current was maintained at 3−4 μA with a potential of approximately 3.5 kV at the needle point and a gap distance of 0.8 cm, while the optimized poling temperature was kept for a certain period of time. The sample was then cooled down to room temperature in the presence of a poling field. The SHG measurements were carried out with a Nd:YAG laser operating at a repetition rate of 10 Hz and a pulse width of 8 ns at 1064 nm. The Y-cut quartz crystal was used as a reference.

3. Results and discussion

3.1. Preparation and characterization

DR19 was synthesized according to the classic route of diazotization-coupling reaction. As shown in Scheme 1, the hyperbranched polymers were synthesized by solution polycondensation through an "A$_2$ + B$_3$" approach. The polymerization was carried out with DR19 as an A$_2$ monomer and BTC as a B$_3$ monomer, TEA as a condensing agent as well. To prepare the hyperbranched polymers in the absence of gelation, a dilute solution of DR19 was slowly added to a dilute solution of BTC at 0−5 °C [23,24]. At the end of polymerization, methanol was used to consume the terminal carboxylic acid chloride groups to afford hyperbranched polymer P1. To prepare the thermally cross-linkable hyperbranched polymer P2, during the final stage of polymerization, free carboxylic acid chloride groups were partially end-capped with 2,3-epoxy-1-propanol, then the residual carboxylic acid chloride groups were quenched with water. The resulting P1 and P2 both were soluble in common organic solvents such as THF, DMF, and DMSO. The ^{1}H NMR spectra in Fig. 1 confirm the molecular structures of P1 and P2. From the spectrum of P2, the presence of multiplet at 2.67, 2.92 and 3.25 ppm corresponds to the protons of epoxy ring, indicating the presence of epoxy terminal groups. The peak appearing at 13.58 ppm is assigned to the hydroxylic protons of carboxylic acid groups.



Scheme 1. Synthetic route of hyperbranched polymer P2.

In the FTIR spectrum of P2 in Fig. 2, the absorption bands at 903 and 3430 cm^{-1} also indicate the presence of epoxy and carboxyl acid groups, respectively.

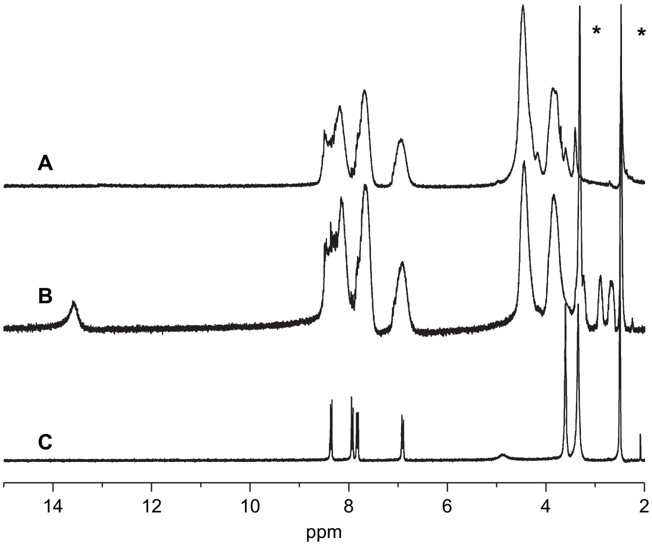


Fig. 1. ^{1}H NMR spectra of (A) P1, (B) P2, and (C) DR19.

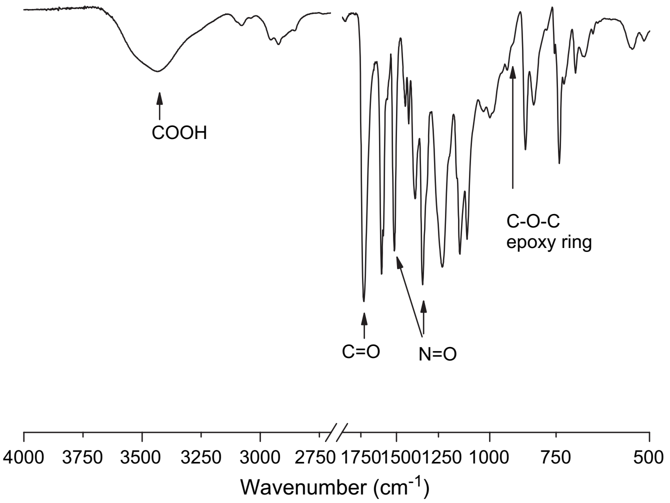


Fig. 2. Typical FTIR spectrum of P2.

The number average molecular weight and polydispersity indices of P1 and P2 were determined with GPC using linear polystyrenes as calibration standards. The results are summarized in Table 1. The molecular weights are expected to be lower than practical ones because of the smaller radius of chain gyration of hyperbranched polymers in comparison with linear counterparts [25,26]. Therefore, the actual molecular weights may be higher than the experimental results.

Fig. 3 shows the UV–vis spectra of P1 and P2, as well DR19 in THF. The absorbance at 283 and 461 nm is attributed to the π–π* transition of their benzene and azobenzene chromophores, respectively. From Table 1, the maximum absorption wavelengths for P1 and P2 in both THF and DMF solutions are blue-shifted more than 28 nm, compared to those of free chromophore molecules (DR19). It is because the chromophores in hyperbranched polymers are surrounded by bulky aromatic esters to probably achieve large site-isolation effect, which can decrease the intermolecular electrostatic interaction between the chomophores and maintain a stable dipole alignment during the poling process [7,27]. By the UV–vis spectroscopic analysis, the chromophore content in both hyperbranched polymers was determined to be at around 50 wt%, which is close to the feed ratio of 53 wt% by calculation.

Table 1
Molecular weights and optical properties of the hyperbranched polymers

Polymer	Yield (%)	M_n[a]	M_w/M_n[a]	λ_{max}[b] (nm)	l_s[c] (μm)	T_p[d] (°C)	d_{33}[e] (pm/V)
P1	49.5	8304	1.28	460 (474)	0.23	130	51
P2	52.4	9027	1.25	461 (474)	0.31	150	59

[a] Determined by GPC in DMF on the basis of a polystyrene calibration.

[b] The maximum absorption wavelength of polymer solutions in THF, while the maximum absorption wavelength of their diluted solutions in DMF is given in parentheses.

[c] Thickness of polymer film.

[d] Poling temperature of polymer film.

[e] Second-harmonic generation coefficient.

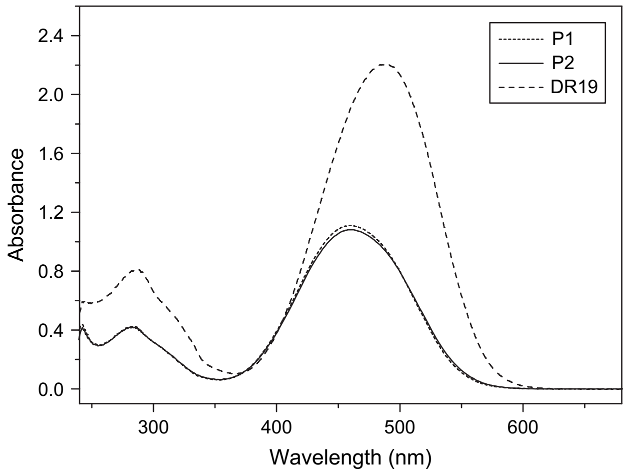


Fig. 3. UV–vis spectra of P1, P2 and DR19 in THF (20 μg/mL).

The thermal behaviors of P1 and P2 were investigated by differential scanning calorimeter (DSC) (Fig. 5) and thermogravimetric analysis (TGA) (Fig. 4). The curve A in Fig. 5 indicates that the T_g of P1 is 135 °C. The curve B shows an exothermic peak starting from approximately 100 °C and peaking at 150 °C, which is due to the cross-linking reaction between epoxy and carboxylic acid groups of P2. Therefore, the poling temperature was set for P2 thin films at 150 °C. The T_g of the cross-linked P2 film was determined to be 164 °C according to curve C. The polymers show thermal stability up to 225 °C from the TGA thermograms. The 5% weight loss temperatures of P1 and P2 are 225 and 243 °C, respectively.

3.2. Nonlinear optical property of hyperbranched polymers

To evaluate the nonlinear optical properties of P1 and P2, their poled thin films were fabricated. The most convenient

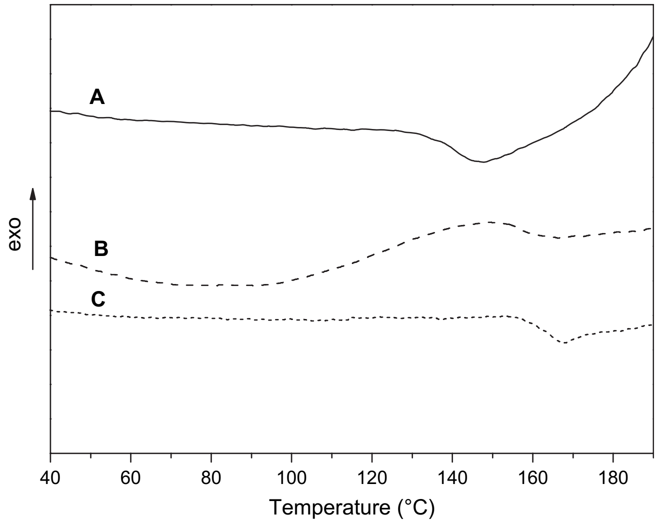


Fig. 4. DSC curves of (A) P1, the second heating, (B) P2, the first heating, and (C) P2, the second heating (nitrogen, 10 °C/min).

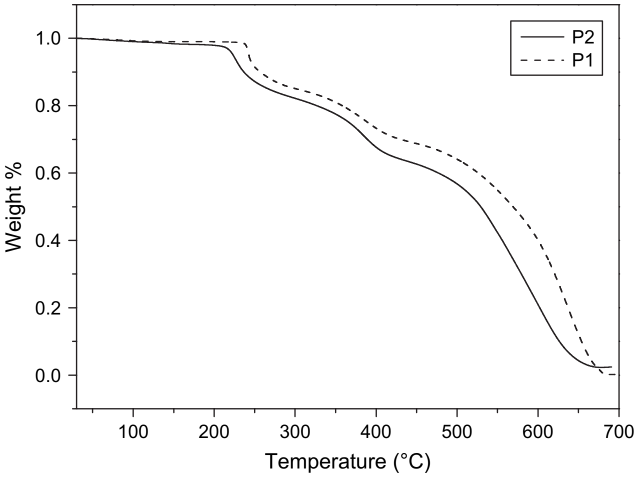


Fig. 5. TGA profiles of P1 and P2 (nitrogen, 10 °C/min).

technique for measuring the second-order NLO activity is to investigate the SHG process characterized by d_{33} value, which can be calculated from the equation for a poled film [28]:

$$\frac{d_{33,\mathrm{s}}}{d_{11,\mathrm{q}}}=\sqrt{\frac{I_\mathrm{s}}{I_\mathrm{q}}}\frac{l_{\mathrm{c,q}}}{l_\mathrm{s}}F \tag{1}$$

where $d_{11,\mathrm{q}}$ is the d_{11} of the quartz crystal (0.45 pm/V), I_s and I_q are the respective SHG intensities of the sample (polymer film) and the quartz crystal, $I_{\mathrm{c,q}}$ is the coherent length of the quartz crystal (20.6 μm), l_s is the thickness of the sample, and F is the correction factor of the apparatus (1.2 when $l_\mathrm{c} \gg l_\mathrm{s}$). According to the equation, the d_{33} values of P1 and P2 were calculated to be 51 and 59 pm/V, respectively, at the fundamental wavelength of 1064 nm. The high SHG coefficients indicate that P1 and P2 possess good optical nonlinearity, thanks to the three-dimensional spatial isolation of their highly branched structure.

For the purpose of evaluating the temperature at which the dipolar relaxation or loss of SHG signal is initiated, a dynamic, thermally induced relaxation experiment was performed. The SHG signals were monitored as the poled films were heated at a rate of 5 °C/min in the absence of poling field. The resulting data were normalized and plotted against one another. Fig. 6 shows that the onset decay temperatures (T_d) of P1 and P2 are approximately 130 and 154 °C, respectively, which indicate that P2 exhibits better dynamic thermal stability than P1. It is suggested that the thermal curing of a polymer may play an important role in enhancing the resistance against the thermal depoling. The epoxy and carboxylic acid end groups of P2 readily undergo thermal cross-linking reaction by moderate heating [29,30]. The resultant thermosetting network can hamper the thermal depoling process.

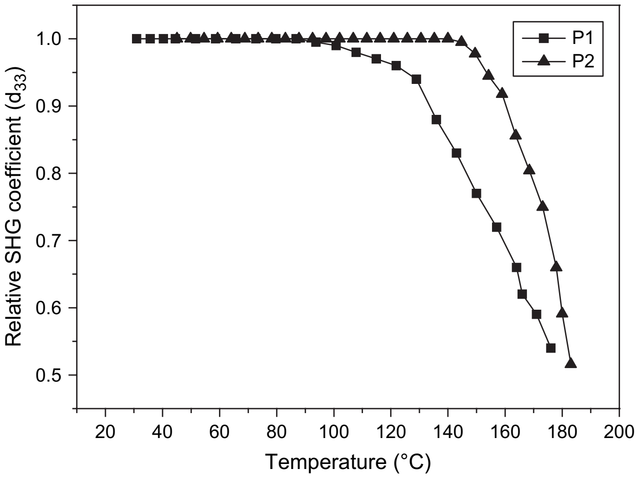


Fig. 6. Decays of SHG coefficients of P1 and P2 as a function of temperature.

4. Conclusion

In this work, two new hyperbranched polymers containing common azobenzene as a NLO active moiety were successfully synthesized through an “$A_2 + B_3$” approach. The hyperbranched polymers exhibit good NLO properties due to the three-dimensional spatial isolation from the highly branched structure. P2 containing epoxy groups exhibit better dynamic thermal stability than P1, thanks to the thermoset network which can resist the thermal depoling. The synthesized hyperbranched polymers may thus become promising candidates for NLO materials with good macroscopic EO activity.

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