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Preparation and nonlinear optical characterization of a novel hyperbranched poly(aryl ether ketone) end-functionalized with nickel phthalocyanine

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Abstract

A novel, hyperbranched poly(aryl ether ketone) end-functionalized with nickel phthalocyanine was prepared using 1,3,5-tris[4-(4-fluorobenzoyl)phenoxy]benzene as ‘core’ molecule, 4,4′-(hexafluoroisopropylidene)diphenol as an A_2 monomer and nickel phthalocyanine as an end-capping reagent. The polymer displayed good solubility and thermal stability; its third order nonlinear optical susceptibility reached as $\approx 10^{-11}$ esu measured using *Z*-scan measurement at 532 nm.

Keywords: Phthalocyanine polymer; Hyperbranched poly(aryl ether ketone); Third order nonlinear optical property; *Z*-scan

1. Introduction

Nonlinear optical (NLO) materials continue attracting attention because of their potential application in optical devices [1–3]. In metallophthalocyanines there are 18π electrons surrounding the center metal atom with large delocalization to form a two-dimensional π-electron conjugated system. The extensively delocalized two-dimensional π-electron distribution offers the possibility of acting as nonlinear optical materials for metallophthalocyanines [4–6]. Nevertheless, it is difficult for most phthalocyanine compounds to dissolve and to melt, which results in the restriction in their applications. In order to enlarge the scope of their application, an effective method is to prepare a phthalocyanine polymer that possesses better solubility and processibility through introducing a phthalocyanine compound to a polymer.

Various phthalocyanine polymers, for example, stacked polyphthalocyanines for electroconductors [7,8], copolymerized phthalocyanine polymers for photoconductors [9,10], phthalocyanine polymers for catalyzers [11,12], and so on, have already been prepared. These polymers have high T_g and are soluble in common organic solvent. Some metals, such as Cu, Zn, Fe, Ni and Co were used in the above preparation.

The basic requirements for good nonlinear optical materials are to possess good solubility and high NLO chromophore density, whereas hyperbranched polymer just has highly branched structure and a number of end groups. Therefore we focus our attention on the synthesis of a novel hyperbranched poly(aryl ether ketone) end-functionalized with nickel phthalocyanine (Pc-HPAEK) based on 1,3,5-tris[4-(4-fluorobenzoyl)phenoxy]benzene (B_3) as a ‘core’ molecule, 4,4′-(hexafluoroisopropylidene) diphenol as an A_2 monomer and nickel phthalocyanine as an end-capping reagent in the present work. Moreover the nonlinear optical property of the obtained Pc-HPAEK was characterized.

2. Experimental

2.1. Materials

Phloroglucinol, 4,4′-(hexafluoroisopropylidene)diphenol (6F-BPA), phthalonitrile and 4-nitritephthalonitrile (Aldrich

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Chemicals Inc.), tetramethylene sulfone (TMS, Dalian Jinzhou Chemical), *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF), toluene, chloroform ($CHCl_3$), ethanol, methanol, acetone, quinoline, potassium carbonate (K_2CO_3) and concentrated hydrochloric acid (36%) were obtained from commercial sources and used as received. 4,4′-difluorobenzophenone was prepared in our lab according to the standard procedure.

2.2. Measurement

Mass spectra (MS) were performed on an AXIMA-CFR laser desorption ionization flying time spectrometer (COMPACT). IR spectra (KBr) were measured on a Nicolet Impact 410 Fourier transform infrared spectrometer. ^1H NMR spectra were recorded on a Bruker 510 NMR spectrometer (500 MHz) with tetramethylsilane as a reference. Gel permeation chromatograms (GPC) using polystyrene as a standard were obtained on a Waters 410 instrument with THF as an eluent at a flow rate of 1 mL min^{-1}. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC821^e instrument at a heating rate of 10 °C min^{-1} under nitrogen. Thermal gravimetric analyses (TGA) were determined in nitrogen atmosphere using a heating rate of 10 °C min^{-1} and polymers were contained within open aluminum pans on a PERKIN ELMER TGA-7. UV absorption spectra were recorded on a Shimadzu UV 2501-PC spectrophotometer in $CHCl_3$ solution at room temperature.

The nonlinear optical property of the sample was characterized by *Z*-scan technique performed with a Q-switched ns Nd:YAG laser system (Surelite II-10) continuum with pulse width of 4.5 ns at 1 Hz repetition rate and 532 nm wavelength. Moreover, the diameter of the light beam passing through the sample was 52 μm. The experiment was set up as in [13]. The solution of the sample of 3.33 mg/ml in DMF was contained in a 2-mm quartz cell. The relation between the normalized transmittance $T(z)$ and z position was obtained by moving the samples along the axis of the incident beam (z-direction) with respect to the focal point. The incident and transmitted energies were detected simultaneously by an energy meter (Laser Probe Corporation, Rj-7620 ENERGY RATIOMETER, RjP-735). The input energy was 43.7 μJ/pulse.

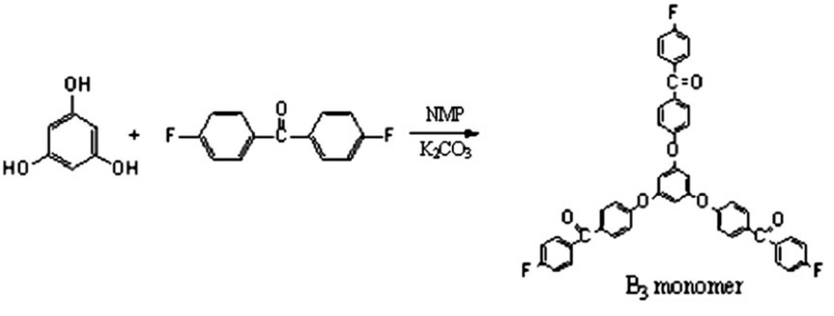
2.3. Synthesis

2.3.1. Synthesis of 1,3,5-tris[4-(4-fluorobenzoyl)phenoxy] benzene (B_3 monomer)

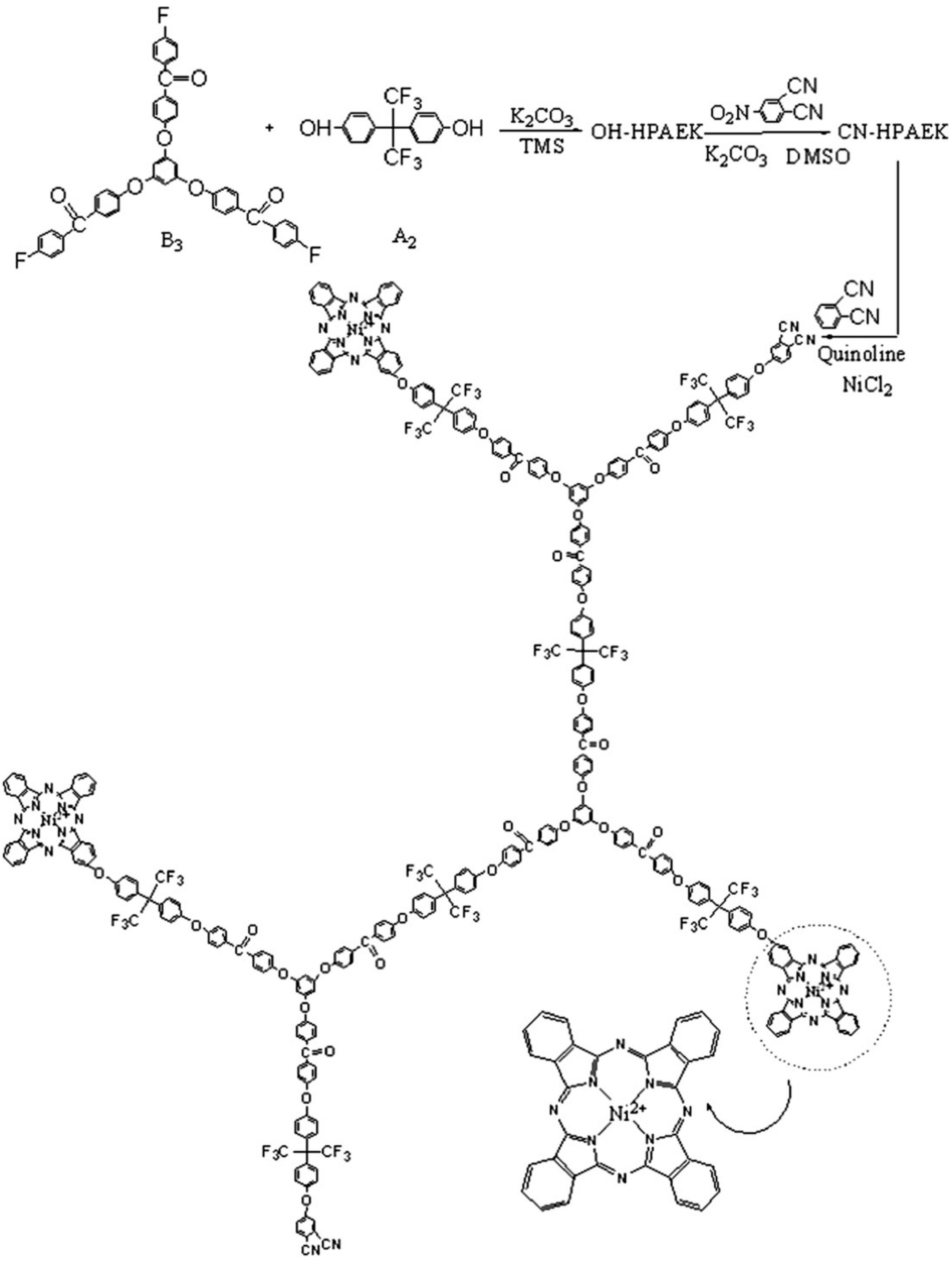
Phloroglucinol (10.08 g, 0.08 mol), 4,4′-difluorobenzophenone (210 g, 1.12 mol), and K_2CO_3 (20 g, 0.15 mol) were dissolved in NMP (500 mL) and toluene (130 mL) in a 1000 mL three-necked flask fitted with a nitrogen inlet, a thermometer, a Dean–Stark trap, and a mechanical stirrer, and the apparatus was purged with nitrogen. The reaction mixture was refluxed at 140–160 °C for 6 h to ensure complete dehydration. After removing toluene, the reaction mixture was heated to 170–190 °C for 4 h under a nitrogen atmosphere. After being poured into a mixture of deionized water (2 L) and hydrochloric acid (50 mL) under vigorous stirring, the precipitate was collected by filtration. The crude product was washed with deionized water and ethanol to give white powder. Yield: 30%; Mp: 131 °C; MALDI-TOF MS: $m/z = 721$; IR (KBr, cm^{-1}): 1656 (–C=O), 1238 (–O–); ^1H NMR ($CDCl_3$): $\delta = 6.61$ (s, 1H), 7.13 (d, 2H), 7.17(t, 2H), 7.81 (d, 2H), 7.83(d, 2H).

2.3.2. Synthesis of hydroxyl-terminated hyperbranched poly(aryl ether ketone) (OH-HPAEK)

B_3 monomer (7.21 g, 0.01 mol), 6F-BPA (10.2312 g, 0.03045 mol), and K_2CO_3 (4.4122 g, 0.03623 mol) dissolved in TMS (58 mL) and toluene (15 mL) in a 250 mL three-necked flask fitted with a nitrogen inlet, a thermometer, a Dean–Stark trap, and a mechanical stirrer, and the apparatus was purged with nitrogen. The reaction mixture was refluxed at 140–150 °C for 2 h to ensure complete dehydration. After removing toluene, the reaction mixture was heated to 170–220 °C for 7 h under a nitrogen atmosphere. After being poured into a mixture of deionized water (500 mL) and hydrochloric acid (8 mL) under vigorous stirring, the precipitate was collected by filtration. The crude product was washed with deionized water and methanol to give pale yellow powder. IR (KBr, cm^{-1}): 3410 (–OH), 1653 (–C=O), 1239 (–O–), 1169 ($-CF_3$); ^1H NMR(DMSO-d_6): $\delta = 6.35$ (br, HO–*Ph*–(O)), 6.85 (m, –*Phloroglucinol*–O–Ph– (O)), 6.93–7.30 (br, –*Ph*–O–Phloroglucinol– (O), –*Ph*–O–*Ph*– (O)), 7.30–7.50 (br, –*Ph*–$C(CF_3)_2$–*Ph*– (O)), 7.59–7.89 (br, –*Ph*–CO–*Ph*– (O)), 9.94 (s, *HO*–Ph–).



Scheme 1. Synthesis of B_3 monomer.



Scheme 2. Synthesis of nickel phthalocyanine-terminated hyperbranched poly(aryl ether ketone) (Pc-HPAEK).

2.3.3. Synthesis of cyano-terminated hyperbranched poly(aryl ether ketone) (CN-HPAEK)

CN-HPAEK was prepared from the polymerization of OH-HPAEK (4.8 g), 4-nitritephthalonitrile (1.7658 g, 0.0102 mol), and K_2CO_3 (1.1738 g, 0.0085 mol) dissolved in DMSO (48 mL) in a 100 mL three-necked flask fitted with a nitrogen inlet, a mechanical stirrer, and the apparatus was purged with nitrogen. The mixture stood at room temperature for 24 h under a nitrogen atmosphere. After being poured into deionized water (500 mL), the precipitate was collected by filtration. The crude product was washed with deionized water and methanol to give pale gray powder. IR (KBr, cm^{-1}): 2226 (−CN), 1655 (−C=O), 1244 (−O−), 1168 ($-CF_3$); ^1H NMR(DMSO-d_6): $\delta = 6.85$ (m, −*Phloroglucinol*−O−Ph− (O)), 6.93−7.34 (br, −*Ph*−O−Phloroglucinol− (O), −*Ph*−O−*Ph*− (O)), 7.34−7.50 (br, −*Ph*−$C(CF_3)_2$−*Ph*− (O)), 7.64−7.89 (br, −*Ph*−CO−*Ph*− (O)), 7.52, 7.95, 8.15 (*Phthalonitrile*−O−).

2.3.4. Synthesis of nickel phthalocyanine-terminated hyperbranched poly(aryl ether ketone) (Pc-HPAEK)

Pc-HPAEK was prepared from the polymerization of CN-HPAEK (0.8 g), phthalonitrile (0.5340 g, 0.0042 mol), and nickel chloride (0.3310 g, 0.0014 mol) dissolved in quinoline (48 mL) in a 100 mL three-necked flask. The procedure was similar to the synthesis of CN-HPEK, except that the reaction mixture was heated at 170–180 °C for 6 h. UV ($CHCl_3$): $\lambda_{max} = 666$ nm.

3. Results and discussion

3.1. Synthesis and characterization

The B_3 monomer (FBPB) was synthesized by nucleophilic substitution of 4,4′-difluorobenzophenone with phloroglucinol in the presence of K_2CO_3. The structure of FBPB is shown in Scheme 1 and confirmed by MS, IR and ^1H NMR. IR spectrum shows characteristic bands of $-C{=}O$ and $-O-$ stretching vibrations at 1656 cm^{-1} and 1238 cm^{-1}, respectively.

The hydroxyl-terminated hyperbranched poly(aryl ether ketone) (OH-HPAEK) was synthesized by nucleophilic substitution polycondensation reaction from 1,3,5-tris[4-(4-fluorobenzoyl)phenoxy]benzene (FBPB) and 4,4′-(hexafluoroisopropylidene)diphenol (6F-BPA), as shown in Scheme 2. The polymerization was carried out in TMS with potassium carbonate as a base catalyzer and by using toluene for dehydration. The number-average molecular weight (M_n) was 4.82×10^3 ($M_w/M_n = 1.52$, GPC measurement), which indicated successful polymerization. The chemical structure of OH-HPAEK was confirmed by IR and ^1H NMR. The IR spectrum shows characteristic absorption bands of $-OH$, $-C{=}O$, $-O-$ and $-CF_3$ at 3410, 1653, 1239 and 1169 cm^{-1}, respectively (Fig. 1a), which suggests that OH-HPAEK has been obtained successfully. Fig. 2a shows the signal assignments of ^1H NMR spectrum of OH-HPAEK in DMSO. Although the signals in the ^1H NMR spectrum of OH-HPAEK were greatly overlapped, the signals corresponding to the proton of $-OH$ group (δ, 9.94) and the proton of located at *ortho*-position of $-OH$ group (δ, 6.35) departed obviously from other protons and could be easily distinguished, which further confirmed the structure of OH-HPAEK.

The cyano-terminated hyperbranched poly(aryl ether ketone) (CN-HPAEK) was prepared from the polymerization of OH-HPAEK and 4-nitritephthalonitrile, as shown in Scheme 2. The number-average molecular weight (M_n) of CN-HPAEK was 6.74×10^3 and $M_w/M_n = 1.47$. The chemical structure of CN-HPAEK was proved by IR and ^1H NMR. The IR spectrum shows characteristic absorption bands of $-CN$, $-C{=}O$, $-O-$ and $-CF_3$ at 2226, 1655, 1244 and 1168 cm^{-1}, respectively (Fig. 1b), which suggests that CN-HPAEK has been obtained successfully. Fig. 2b shows the signal assignments of ^1H NMR spectrum of CN-HPAEK in DMSO. The signals corresponding to the proton of $-OH$ group (δ, 9.94) and the proton of located at *ortho*-position of $-OH$ group (δ, 6.35) in ^1H NMR spectrum of OH-HPAEK were visible, while the above-mentioned signals disappeared and some new signals corresponding to the three protons near $-CN$ groups (δ, 7.52, 7.95, 8.15) in Fig. 2b appeared, which further proved the structure of CN-HPAEK.

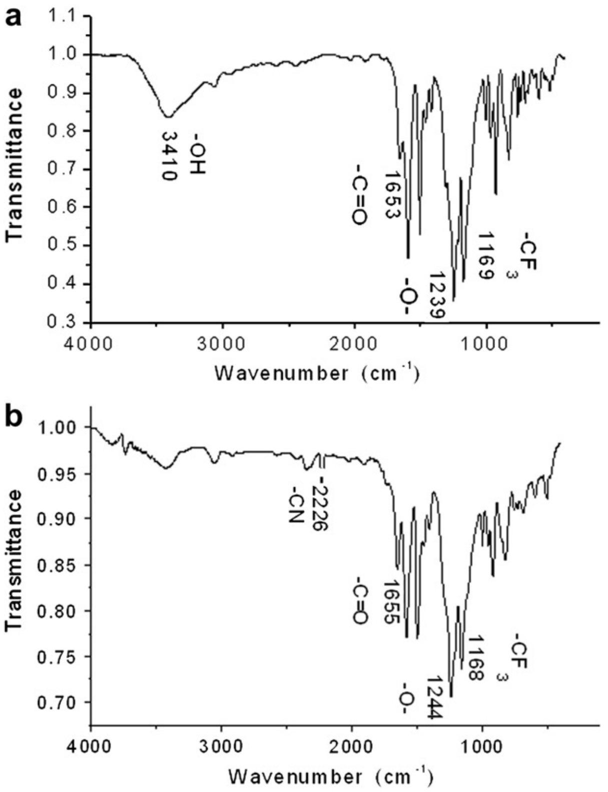


Fig. 1. IR spectrum of (a) hydroxyl-terminated hyperbranched poly(aryl ether ketone) (OH-HPAEK) and (b) cyano-terminated hyperbranched poly(aryl ether ketone) (CN-HPAEK).

The nickel phthalocyanine-terminated hyperbranched poly(aryl ether ketone) (Pc-HPAEK) was prepared from the polymerization of CN-HPAEK, phthalonitrile and nickel chloride, as shown in Scheme 2. The number-average molecular weight (M_n) of CN-HPAEK was 6.16×10^3 and $M_w/M_n = 1.41$. A valuable NMR spectrum could not be supplied due to the paramagnetic nickel ion. However, the UV–vis absorption spectrum lent support to the chemical structure of Pc-HPAEK. It is well-known that the best indication for phthalocyanine system is given by their UV–vis absorption spectrum in solution (Fig. 3). The UV–vis absorption spectrum of Pc-HPAEK shows the typical Q band of symmetrical macrocyclic substituted Pc. In the UV–vis absorption spectrum of nickel phthalocyanine-terminated hyperbranched poly(aryl ether ketone) in chloroform, the characteristic spilt Q band is observed with absorptions at 601 and 666 nm. The higher energy peak of Q band is located at 601 nm and is connected with the first $\pi \rightarrow \pi^*$ transition on the phthalocyanine macrocycle. The lower energy peak of Q band is located at 666 nm and is connected with vibrational interval [14] or excitionic transition [15]. The above analysis suggested successful introduction of phthalocyanine group into the polymer end.

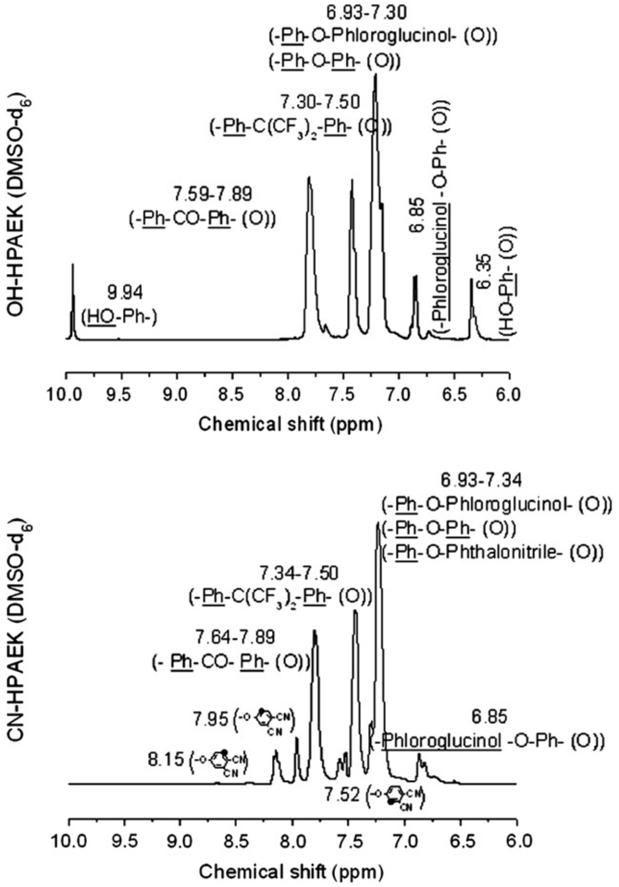


Fig. 2. NMR spectrum of hydroxyl-terminated hyperbranched poly(aryl ether ketone) (OH-HPAEK) and cyano-terminated hyperbranched poly(aryl ether ketone) (CN-HPAEK).

3.2. Solubility and thermal property of Pc-HPAEK

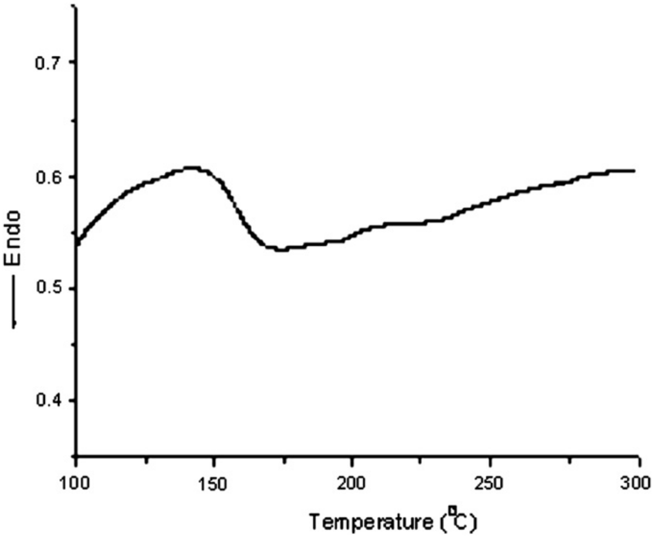


Fig. 4. DSC curve of nickel phthalocyanine-terminated hyperbranched poly (aryl ether ketone) (Pc-HPAEK).

Pc-HPAEK was well soluble in solvents such as $CHCl_3$, THF, DMF, DMAc, DMSO and NMP, but insoluble in ethanol and acetone. The presence of highly branched structure for Pc-HPAEK facilitated solvent molecular to diffuse into solute zone, therefore the solubility could be improved to some degree. The DSC curve of Pc-HPAEK is shown in Fig. 4 and the glass transition temperature (T_g) of Pc-HPAEK is 157 °C. In DSC curve, no other thermal change except T_g was observed below decomposition temperature, indicating that Pc-HPAEK is amorphous. The TGA curve of Pc-HPAEK is shown in Fig. 5 and 5% weight loss temperature of Pc-HPAEK is 451 °C, indicating that Pc-HPAEK possesses good thermal stability due to the aromatic backbone of hyperbranched poly(aryl ether ketone) and phthalocyanine.

3.3. Nonlinear optical property of Pc-HPAEK

The nonlinear coefficients of the polymers were measured by the *Z*-scan technique. *Z*-scan is a well-known technique

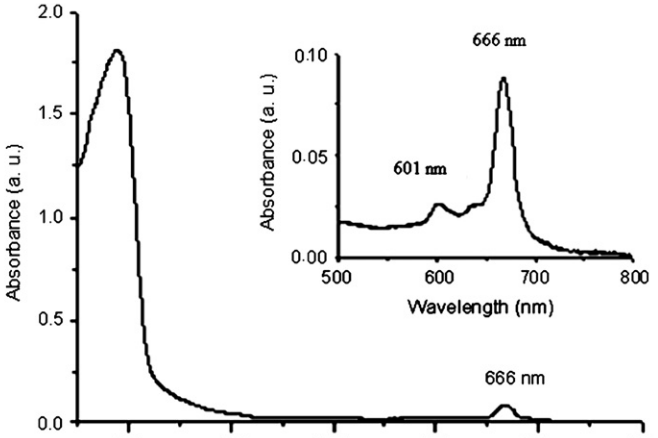


Fig. 3. UV–vis spectrum of nickel phthalocyanine-terminated hyperbranched poly(aryl ether ketone) (Pc-HPAEK) solution in $CHCl_3$.

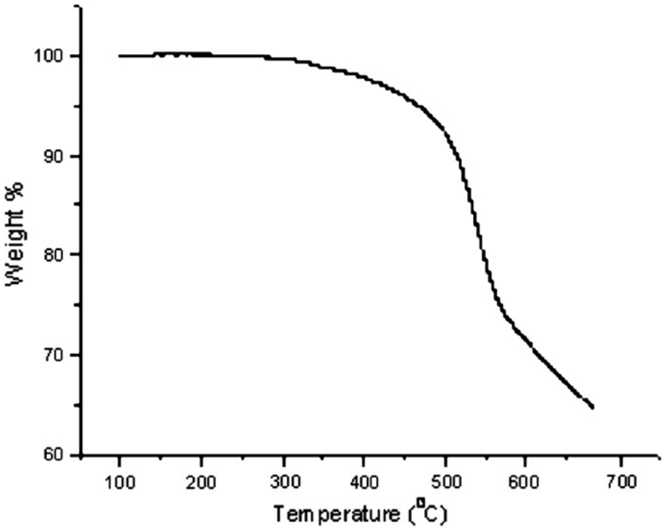


Fig. 5. TGA curve of nickel phthalocyanine-terminated hyperbranched poly (aryl ether ketone) (Pc-HPAEK).

that allows the simultaneous measurement of both nonlinear absorption coefficient (α_2) and the nonlinear refractive coefficient (n_2). The basic idea behind *Z*-scan technique is self-focusing or self-defocusing. A Gaussian beam is focused by a lens onto the sample and the variation in the beam profile is observed at the far field as the sample is taken through the focus of the lens. The beam propagation direction is taken as *z*-direction and hence this technique is known as *Z*-scan technique. By properly monitoring the transmittance change through a small aperture placed at the far field position (closed aperture), one is able to determine the amplitude of the phase shift. By moving the sample through the focus and without placing an aperture at the detector (open aperture), one can measure the intensity dependent absorption as a change of transmittance through the sample.

In our experiment, the sample was moved forward or backward along the direction of the laser beam around the focus ($z = 0$). The transmittance was simultaneously recorded by an energy meter with and without an aperture in the far field of lens as the function of sample position. Fig. 6a shows the normalized transmittance plotted as a function of the sample position (z) measured with an open aperture, thus an intensity dependent absorption effect is observed. The open aperture transmittance, which is symmetric with respect to the focus ($z = 0$), where it has a minimum transmittance, indicates that the nonlinear absorption in Pc-HPAEK is unambiguous. From the linear absorption spectrum of Pc-HPAEK (Fig. 3), the absorption maximum locates at 601 and 666 nm, respectively. The used laser wavelength (532 nm) in our experiment is in the near-resonant absorption region of Pc-HPAEK. Thus the one-photon absorption affects *Z*-scan measurement. In order to minimize the effect of one-photon absorption, the very low repetition rate of 1 Hz was adopted.

The pure nonlinear refraction curve of Pc-HPAEK, shown in Fig. 6b, was obtained by the division of the closed aperture data by the corresponding open aperture data. The *Z*-scan signature shows a large negative nonlinearity (self-defocusing) for Pc-HPAEK. Thus, the third order nonlinear coefficient ($\chi^{(3)}$) of the polymer measured in this experiment was attributed to dual contributions of nonlinear absorption and refraction of the molecules. In theory, the normalized transmittance for the open aperture can be written as [16,17]:

$$T(z, s=1) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}}, \text{ for } |q_0| < 1 \tag{1}$$

where $q_0(z) = \alpha_2 I_0(t) L_{\text{eff}}/(1 + z^2/z_0^2)$, with α_2 as the nonlinear absorption coefficient, $I_0(t)$ as the intensity of laser beam at focus ($z = 0$), $L_{\text{eff}} = [1 - \exp(-\alpha_0 L)]/\alpha_0$ is the effective thickness with α_0 as the linear absorption coefficient and L as the sample thickness, z_0 as the diffraction length of the beam, and z as the sample position. Thus, the nonlinear absorption coefficient α_2 of Pc-HPAEK is determined to be 1.51×10^{-10} m/W by fitting the experiment data using Eq. (1).

The normalized transmission for the closed aperture *Z*-scan is given by [16,17]:

$$T(z, \Delta\Phi) = 1 + \frac{4\Delta\Phi\chi}{(\chi^2 + 9)(\chi^2 + 1)} \tag{2}$$

where $\chi = z/z_0$ and $\Delta\Phi$ is on-axis phase change caused by the nonlinear refractive index of the sample and $\Delta\Phi = [2\pi I_0(1 - e^{-\alpha_0 L})n_2]/(\lambda\alpha_0)$. Thus, the nonlinear refractive coefficient n_2 of Pc-HPAEK is determined to be 3.70×10^{-11} esu by fitting the experimental data using Eq. (2).

The $\chi^{(3)}$ can be calculated by the following equation [16,17]:

$$|\chi^{(3)}| = \sqrt{\left|\frac{cn_0^2}{80\pi} n_2\right|^2 + \left|\frac{9 \times 10^8 \varepsilon_0 n_0^2 c^2}{4\pi\omega} \alpha_2\right|^2} \tag{3}$$

where ε_0 is the permittivity of vacuum, c is the speed of light, n_0 is the refractive index of the medium and $\omega = 2\pi c/\lambda$. Thus,

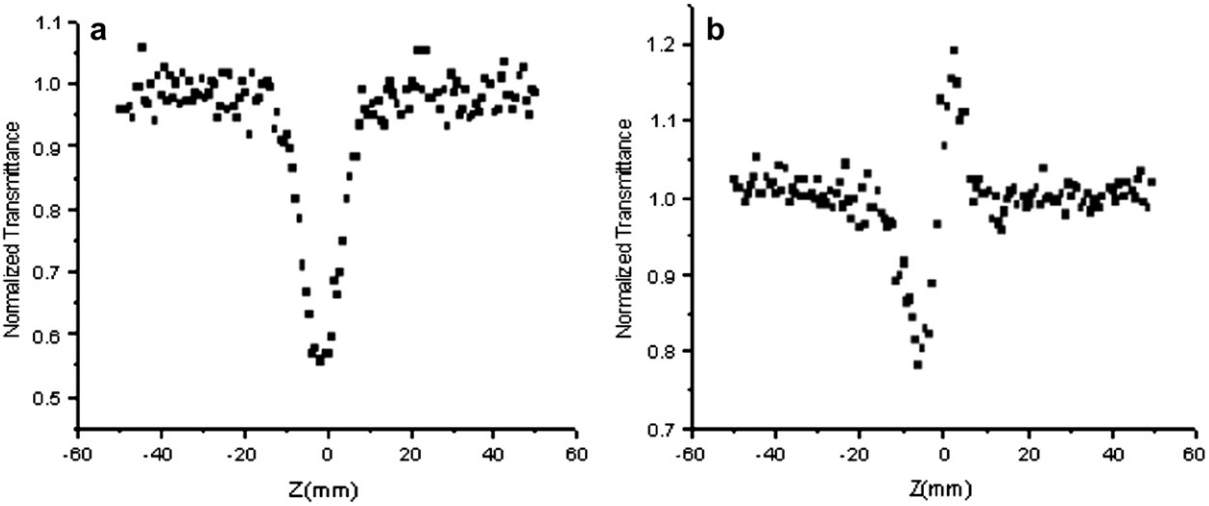


Fig. 6. (a) *Z*-scan data of opened aperture and (b) *Z*-scan data of closed aperture for nickel phthalocyanine-terminated hyperbranched poly(aryl ether ketone) (Pc-HPAEK).

the nonlinear susceptibility $\chi^{(3)}$ of Pc-HPAEK is determined to be 0.98×10^{-11} esu, which is almost five times larger than that of some metallophthalocyanines [18,19].

4. Conclusions

A novel hyperbranched poly(aryl ether ketone) end-functionalized with nickel phthalocyanine (Pc-HPAEK) was prepared by using 1,3,5-tris[4-(4-fluorobenzoyl)phenoxy]benzene (B_3), as a 'core' molecule, 4,4′-(hexafluoroisopropylidene)diphenol (6F-BPA) as an A_2 monomer, and nickel phthalocyanine as an end-capping reagent. The obtained Pc-HPAEK possesses good solubility, high glass transition temperature, high decomposition temperature and large third order NLO coefficient due to highly branched structure, the aromatic backbone and a number of functionalized end groups. Such a novel nickel phthalocyanine-functionalized HPAEK is expected to be a potential candidate for optical applications.

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