

Specific Thermoresponsive Behaviours Exhibited by Optically Active and Inactive Phenylalanine Modified Hyperbranched Polyethylenimines in Water^{*}

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Abstract Optically active and inactive hyperbranched polymers with specific thermoresponsive behaviours in water were reported. Through two steps hyperbranched polyethylenimine (HPEI) polymers terminated with different amount of D-phenylalanine (D-Phe), L-phenylalanine (L-Phe) or DL-phenylalanine (DL-Phe) were prepared and characterized. The analyses on the solution properties by turbidimetry, dynamic light scattering, fluorescence probe and ¹H-NMR demonstrated that all the polymers exhibited specific thermoresponsive behaviours in water, including: (1) In the dilute polymer concentration region, increasing the polymer concentration led to the increase of phase transition temperature; (2) The optically inactive thermoresponsive hyperbranched polymers showed a higher cloud-point temperature (T_{cp}) than their corresponding optically active ones in a relatively higher polymer concentration; (3) At the same polymer concentration the hydrophobic groups of the optically inactive HPEI-DL-Phe formed more perfect hydrophobic domain than those of the optically active HPEI-L-Phe and HPEI-D-Phe.

Keywords Hyperbranched; Polyethylenimine; Thermoresponsive; Phenylalanine; Optically active

Electronic Supplementary Material Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s10118-017-1950-5>.

INTRODUCTION

During the past decade, polymers with stimuli-responsive properties, such as fast and reversible conformational or phase changes in response to variations in temperature or pH have gained much interest in many aspects^[1, 2]. One of the most appealing stimuli-responsive species is the thermoresponsive hydrophilic polymer having the lower critical solution temperature (LCST) in aqueous medium, which means that above a specific temperature its solubility in water dramatically decreases^[3].

With respect to thermoresponsive polymers, LCST control is a very important issue in their design and practical applications. Normally, the LCSTs of thermoresponsive polymers can be modulated through varying the ratio of hydrophilic and hydrophobic units, and the more hydrophilic one shows a higher LCST than the more hydrophobic counterpart^[3]. Varying the ratio of hydrophilic and hydrophobic units can be realized by

^{*} This work was financially supported by the National Natural Science Foundation of China (Nos. 20804027 and 21274106) and Shanghai Key Laboratory of Magnetic Resonance.

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Received February 14, 2017; Revised March 22, 2017; Accepted March 27, 2017

doi: 10.1007/s10118-017-1950-5

many strategies, such as introducing other hydrophilic or hydrophobic units to the polymers^[4–7], adjusting the pH of the polymer solution^[8, 9], adding inorganic salts^[10, 11], irradiating with light^[12–14], formation of supramolecular complexes^[14–19] and so on. Beyond the well-known hydrophilic/hydrophobic modulation method, recently, topology alteration^[20–25] and stereochemical effect^[26–29] were also found to have influence on LCST. For instance, it was found that cyclic poly(*N*-isopropylacrylamide) (PNIPAM) exhibited a higher cloud point than the linear counterpart at the low polymer concentration, whereas their cloud points were similar at the high polymer concentration^[21, 22]. Aoki *et al.*^[26] and Seto *et al.*^[27] found that an optically active polymer showed a lower cloud point than the optically inactive one. Two acid-labile poly(methacrylamide)s with the pendant cyclic orthoester moieties of *trans* and *cis* configurations were reported to exhibit different thermoresponsive behaviour in water^[28]. Two polymers with different pyrrolidone-based side groups had been addressed to show different thermoresponsive phase transition behaviours due to the different steric hindrance effects of their side groups^[29].

Up to the present date, thermoresponsive dendritic polymers containing optically active units are very scarce^[30]. Herein, we prepared a series of optically active and inactive thermoresponsive hyperbranched polymers. All of them exhibited specific thermoresponsive behaviours in water.

EXPERIMENTAL

Materials

Hyperbranched polyethylenimine (HPEI, Aldrich, $M_n = 1.0 \times 10^4$ Da) was dried under vacuum prior to use. L-phenylalanine (L-Phe, 99%), D-phenylalanine (D-Phe, 99%) and DL-phenylalanine (DL-Phe, 99%) were purchased from Tianjin Guangfu Fine Chemical Research Institute and used after recrystallization in the mixture of water and ethanol (1/1, *V/V*). Triethylamine (TEA, A.R.) and dimethyl sulfoxide (DMSO, A.R.) were purchased from Tianjin Kewei Chemical Company and were purified by distillation prior to use. *N*-hydroxysuccinimide (NHS, 99%) and 1-ethyl-3-[3-(dimethylamino)propyl] carbodiimide hydrochloride (EDC, 99%) were purchased from Aladdin Industrial Corporation. Di-*tert*-butyl dicarbonate was obtained from Tianjin Heowns Biochem Company. Acetyl chloride (99%) was purchased from Alfa Aesar. *N*-(*tert*-butoxycarbonyl)-phenylalanine (Boc-Phe) was prepared according to the literature^[31].

Syntheses of Phe-modified HPEI

A typical procedure was as follows: TEA (0.50 mL), EDC (0.29 g, 1.5 mmol) and DMSO (5.0 mL) were mixed together and were treated by ultrasonication for 5 min. Subsequently, NHS (0.17 g, 1.5 mmol) and Boc-Phe (0.27 g, 1.0 mmol) were added and stirred at room temperature for 1 h. HPEI (0.13 g) in DMSO (2 mL) was added to the above solution containing the activated Boc-Phe and the mixture was stirred at 30 °C for 60 h under nitrogen atmosphere. The Boc-Phe-modified HPEI was precipitated from DMSO into distilled water. The obtained Boc-Phe-modified HPEI was treated with the methanol solution of HCl (10%, 10 mL) at 40 °C for 3 h to remove Boc groups. Then, the mixture was concentrated under vacuum and diluted with methanol (10 mL) for three cycles until the residues could be totally dissolved in 6 mL of methanol. The mixture was twice precipitated from methanol solution into anhydrous chloroform. The obtained Phe-modified HPEI product was further purified by dialysis against deionized water, and was subsequently dried in a vacuum freezing drier for 24 h. Yield: 60%. Other Phe-modified HPEI products were prepared by the same procedure.

Characterization

¹H-NMR spectra were recorded on a Bruker 700 MHz spectrometer. Elemental analysis was performed on an Elementar Vario ELCUBE. The specific optical rotations were measured using Autopol IV automatic polarimeter. Dynamic light scattering (DLS) measurements were performed using the Malvern Nano ZS instrument with 633 nm He-Ne laser light, and the light collection at 90°.

Turbidity Measurement

Light transmittance of the phosphate-buffered saline (PBS) solution of the polymer was measured on a temperature-controlled Purkinje General (China) T6 UV/Vis Spectrophotometer at 660 nm, and the heating rate was 0.5 K/2min or 0.2 K/2min. The cloud-point temperature (T_{cp}) was taken from the intersection of the

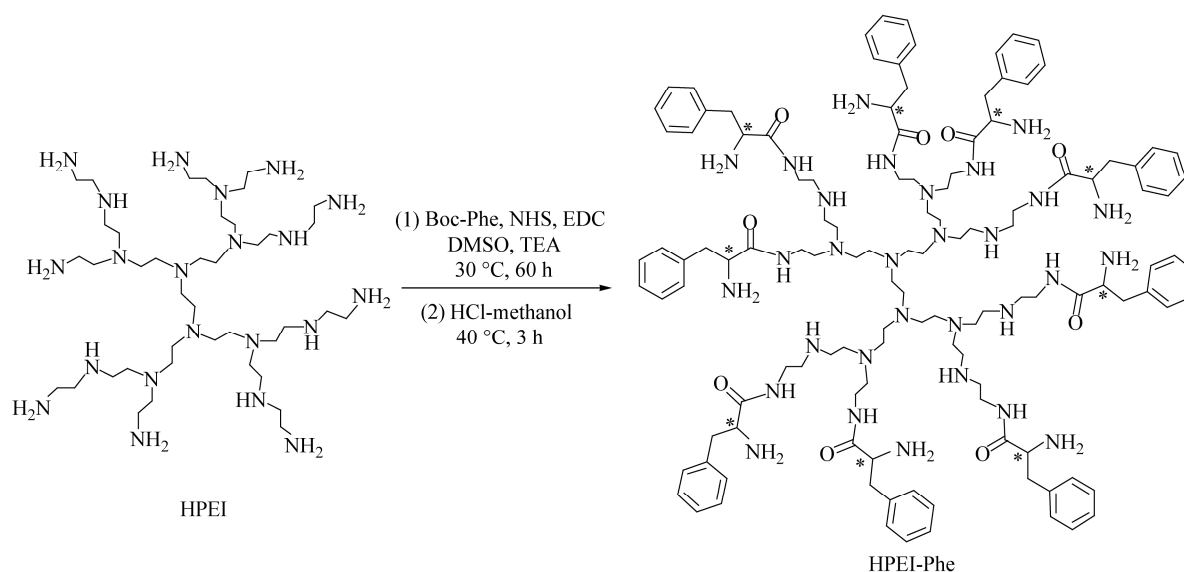
maximal slope tangent and the initial horizontal tangent in the resulting transmittance versus temperature curve. The temperature error is ± 0.1 °C.

Fluorescence Measurement

A Hitachi F-2500 fluorescence spectrometer was used for the fluorescence measurements. Excitation was set at 330 nm and emissions were recorded in the wavelength range of 345–500 nm with a scanning rate of 240 nm/min. The slit widths for both excitation and emission were fixed at 2.5 nm. Fifty microliter of ethanol solution of pyrene (2.4×10^{-5} mol/L) was added into a 5.00 mL volumetric flask, and the solvent was evaporated at 60 °C. Then, PBS containing different amounts of polymer (1.0×10^{-3} mg/mL to 4.0 mg/mL) was added to the flask. After being sonicated for 2 h, the polymer solutions in flask were equilibrated for 2 days at 4 °C in a refrigerator. The final pyrene concentration in all of the polymer solutions was 4.0×10^{-7} mol/L. All measurements were performed at room temperature.

RESULTS AND DISCUSSION

Optically active and inactive HPEI derivatives were prepared in two steps (Scheme 1). First, HPEI was modified with Boc-Phe activated by NHS and EDC. The resulting polymer was designated as HPEI-Boc-Phe. Subsequently, the Boc groups of HPEI-Boc-Phe were deprotected by the methanol solution of HCl (10%), resulting in the Phe modified HPEI (HPEI-Phe). Boc-D-Phe and Boc-L-Phe were used for the syntheses of optically active polymers, HPEI-D-Phe and HPEI-L-Phe, respectively. Boc-DL-Phe was used for the synthesis of optically inactive polymer, HPEI-DL-Phe.



Scheme 1 Preparation of thermoresponsive HPEI-Phe

The obtained HPEI-D-Phe, HPEI-L-Phe and HPEI-DL-Phe polymers were characterized by the FTIR (Fig. S1 in supporting information, SI). All the spectra show the strong absorptions at 1618 cm^{-1} (C=O stretching) and 1532 cm^{-1} (NH deformation and C–N stretching) that are characteristic for the secondary amide groups, indicating the successful transformation of primary amine groups of HPEIs into amide groups by reacting with the activated carboxylic acid group of Phe. Moreover, other characteristic peaks of the as-prepared polymers can also be seen obviously in all the spectra, such as NH stretching (broad band centered at 3267 cm^{-1}), C–N stretching and N–H bending of secondary amide units (1252 cm^{-1}), C–N stretching of HPEI moiety (1060 cm^{-1}), monosubstituted benzene ring CH wagging (749 cm^{-1}) and benzene ring deformation (700 cm^{-1}). From FTIR spectra, these HPEI-Phe polymers with different chiral center cannot be distinguished.

Subsequently, ^1H -NMR was used to characterize these HPEI-Phes in D_2O . It is clear that increasing the polymer concentration leads to the downfield movement of the chemical shift of the proton connected to the chiral center (around $\delta = 3.9$) and the phenyl protons (doublet between $\delta = 7.0$ – 7.5) of HPEI-Phes (Fig. S2 in SI). At the same polymer concentration, the proton connected to the chiral center shows a different chemical shift (around $\delta = 3.9$) among HPEI-D-Phe, HPEI-L-Phe and HPEI-DL-Phe (Fig. S3 in SI). Moreover, the phenyl protons (doublet between $\delta = 7.0$ – 7.5) also show slight difference in chemical shift.

The quantitative information on all the HPEI-Phes was further interpreted and listed in Table 1. HPEI-L-Phes and HPEI-D-Phes show specific optical rotations of around $+19^\circ$ and -18° , respectively, indicating that they are optical active polymers. From Table 1, it is known that a series of HPEI-Phes with different degree of substitution (DS) of Phe groups in primary amine groups of HPEI can be obtained; however, because of the less reactivity of carboxylic acid as amidation reagent and the obvious steric hindrance effect, it is difficult for DS value to reach almost 100% even when much excess reactants are fed. Moreover, the DS values interpreted from ^1H -NMR are much lower than those from elemental analysis. The integrals of phenyl protons are used for the DS calculation from ^1H -NMR. From the following discussion, it is known that HPEI-Phes in water are normally in aggregated state and the mobility of the hydrophobic phenyl units is reduced, leading to the integral inaccuracy for phenyl units. Therefore, the DS values deduced from elemental analysis are adopted herein.

Table 1 Structural parameters of HPEI-Phes

Polymer	$[\alpha]_{20}^{589}$ ^a ($^\circ$)	DS _(EA) ^b	DS _(NMR) ^c	Nomenclature
1	0	0.59	0.50	HPEI-DL-Phe _{0.59}
2	0	0.66	0.54	HPEI-DL-Phe _{0.66}
3	0	0.73	0.49	HPEI-DL-Phe _{0.73}
4	0	0.78	0.51	HPEI-DL-Phe _{0.78}
5	0	0.82	0.52	HPEI-DL-Phe _{0.82}
6	0	0.88	0.58	HPEI-DL-Phe _{0.88}
7	17.3	0.50	0.46	HPEI-L-Phe _{0.50}
8	20.0	0.65	0.45	HPEI-L-Phe _{0.65}
9	19.2	0.75	0.49	HPEI-L-Phe _{0.75}
10	18.2	0.88	0.56	HPEI-L-Phe _{0.88}
11	-17.8	0.57	0.41	HPEI-D-Phe _{0.57}
12	-19.0	0.68	0.45	HPEI-D-Phe _{0.68}
13	-17.9	0.74	0.51	HPEI-D-Phe _{0.74}
14	-18.8	0.88	0.63	HPEI-D-Phe _{0.88}

^a Measured in distilled water at 589 nm ($c = 1.00$) using a digital polarimeter; ^b DS_(EA) represents the degree of substitution of Phe groups in primary amine groups of HPEI calculated from elemental analysis; ^c DS_(NMR) represents the degree of substitution of Phe groups in primary amine groups of HPEI calculated from ^1H -NMR.

The aqueous solutions of HPEI-Phes become turbid after being heated to certain temperature and become transparent again when the solutions are cooled down, indicating that they are thermoresponsive. For the quantitative analysis, turbidimetry was adopted. Obvious phase transition can be observed in both the heating and cooling processes (Fig. 1a and Fig. S4 in SI). Furthermore, it is observed that the heating and cooling cycles do not overlap and the obvious hysteresis can be attributed to the strong hydrogen-bonds among macromolecules^[32]. The phase transition temperature, here called as the cloud point temperature (T_{cp}), is obtained from the intersection of the maximal slope tangent and the initial horizontal tangent in the heating phase transition curve.

DLS was also used to measure the phase transition behaviour of HPEI-Phe in water (Fig. 1b). Below 20°C , the average hydrodynamic radius (R_h) of particles is *ca.* 13 nm, indicating that HPEI-Phes exist as small aggregates in water. Above 20°C , initially, the R_h value increases slowly, followed by a sharp increase at *ca.* 30°C that is similar to T_{cp} measured by turbidimetry. After 40°C , R_h value has only a slight increase. Upon cooling, initially, R_h decreases slightly compared with that in the heating process, however, obvious hysteresis of

disruption of larger aggregates into smaller ones is observed with the further temperature decrease. This DLS heating and cooling diagrams are in accordance with the heating and cooling cycles observed from turbidimetry. Since the phase transition temperatures interpreted from turbidimetry and DLS are similar, in the subsequent measurements only turbidimetry is adopted.

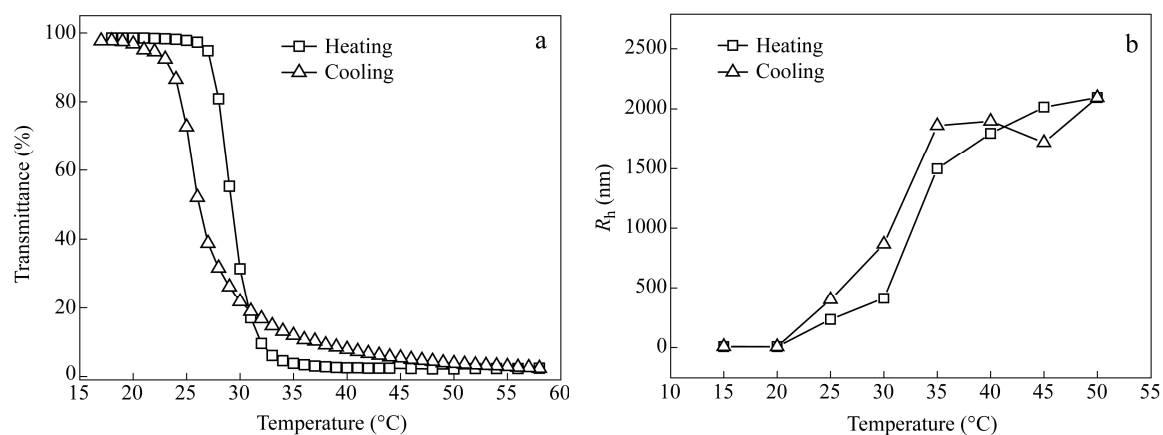


Fig. 1 Typical temperature-dependent (a) light transmittance and (b) R_h variation of HPEI-Phe in water during the heating and cooling process
HPEI-L-Phe_{0.75} as the representative, polymer concentration is 1.0 mg/mL, 0.01 mol/L PBS with pH = 7.4.

Up to the present date, thermoresponsive linear/dendritic polymers ever reported in dilute solution show the similar concentration-dependent phase transition variation trend, *i.e.* initially, phase transition temperature decreases sharply with increasing the polymer concentration, followed by attenuation till level-off^[9, 33–36]. However, specific concentration-dependent T_{cp} variation is observed in all the HPEI-Phes, *i.e.* T_{cp} increases almost linearly with increasing the polymer concentration (Fig. 2). Moreover, HPEI-Phe with less Phe terminals has a higher T_{cp} , indicating that Phe group is relatively hydrophobic. Meanwhile, because of the existence of amine groups, the thermoresponsive property of HPEI-Phe is pH-sensitive, where T_{cp} increases obviously when the solution becomes more acidic (Fig. S5 in SI).

For elucidating this specific concentration-dependent thermoresponsive behaviour, fluorescence technique with pyrene as the hydrophobic probe is used to monitor whether apolar microdomain exists in the solution of HPEI-Phe. The transfer of pyrene from a polar microdomain into a less polar one will lead to the decrease of intensity ratio of pyrene peaks at 373 (I_1) and 383 nm (I_3) in the emission spectra^[37]. From Fig. S6 (in SI), it is clear that, initially, the I_1/I_3 ratio is higher than 1.8 and remains almost constant in the extreme low polymer concentrations, indicating that no apolar microdomain exists. The I_1/I_3 ratio decreases gradually with further increasing the polymer concentration above the critical aggregation concentration (CAC), indicating that less polar environment is gradually formed above CAC. The CACs of all the HPEI-Phes with different Phe content in water are around 0.087 mg/mL, much lower than those used for T_{cp} measurements. Thus, it is clear that HPEI-Phes are in the aggregated state even before T_{cp} , similar to the observation from DLS. From Fig. 3 it is known that in the polymer concentration range for T_{cp} measurements, the I_1/I_3 ratio always decreases with the increase of polymer concentration. The continuous decrease of I_1/I_3 ratio indicates that in the higher polymer concentration, more content of hydrophobic Phe units aggregate together to form more perfect hydrophobic domain to accommodate pyrene probe. Thus, more content of hydrophilic units are stretched out and spread on the surface of polymer aggregates. It is known that varying the spatial distribution of functional units in hyperbranched polymers is an effective method to alter T_{cp} ^[38]. The hyperbranched polymer with hydrophobic units insides exhibits higher T_{cp} than its analogue with hydrophobic units on the surface. Therefore, increasing the polymer concentration leads to the gradual T_{cp} increase of HPEI-Phes. Furthermore, the deduction from fluorescence measurement supports that more perfect hydrophobic domain formation results in more obvious

downfield movement of the chemical shift of proton connected to the chiral center (around $\delta = 3.9$) and the phenyl protons (doublet between $\delta = 7.0$ – 7.5) of HPEI-Phes in water as shown in the ^1H -NMR spectra (Fig. S2 in SI).

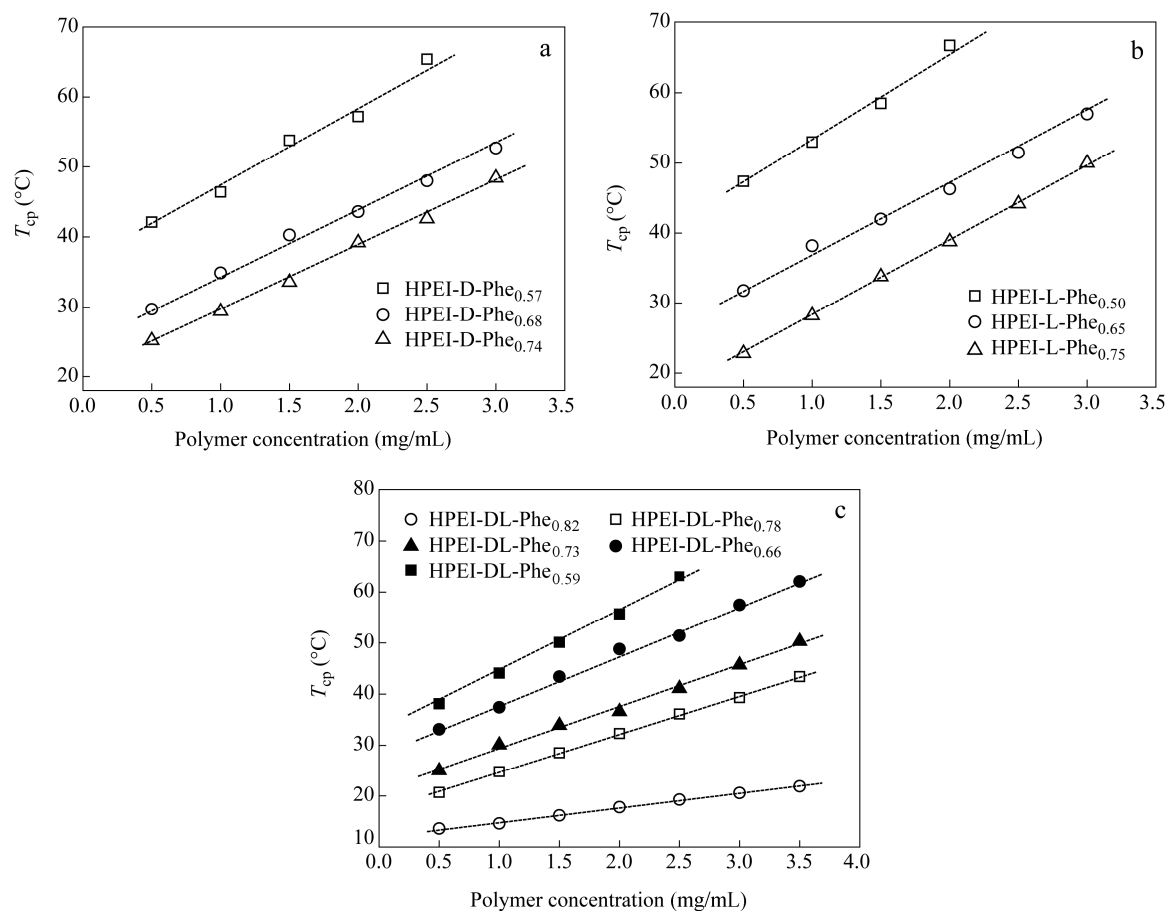


Fig. 2 Typical influence of polymer concentration on T_{cp} of (a) HPEI-D-Phes, (b) HPEI-L-Phes and (c) HPEI-DL-Phes in water (0.01 mol/L PBS with pH = 7.4)

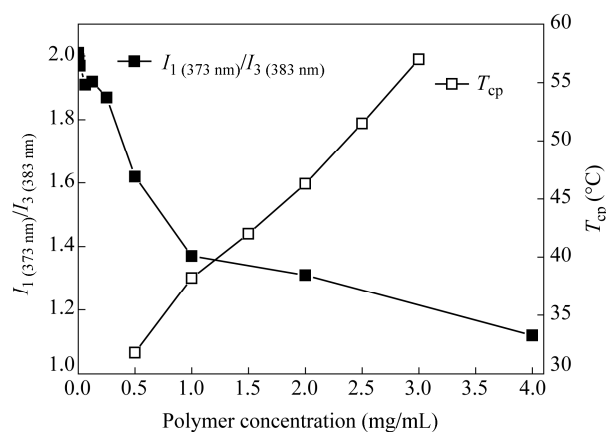


Fig. 3 Comparison of the curves of $I_1(373\text{ nm})/I_3(383\text{ nm})$ versus polymer concentration and T_{cp} versus polymer concentration (HPEI-L-Phe_{0.65} as the representative)

Finally, T_{cp} values of optically active and inactive HPEI-Phe_{0.88} are compared (Fig. 4). The T_{cp} difference between the optically active HPEI-L-Phe and HPEI-D-Phe is minor, but their T_{cp} values become obviously less than the optically inactive HPEI-DL-Phe at relatively higher polymer concentrations. According to the inference from fluorescence measurement, this phenomenon means that at the same polymer concentration the hydrophobic groups of HPEI-DL-Phe form more perfect hydrophobic domain than those of HPEI-L-Phe and HPEI-D-Phe. The ¹H-NMR characterization also supports such reference since the chemical shifts of the proton connected to the chiral center (around $\delta = 3.9$) and the phenyl protons (doublet between $\delta = 7.0$ – 7.5) of HPEI-DL-Phe are greater than those of HPEI-L-Phe and HPEI-D-Phe (Fig. S3 in SI). This is different from the mechanism for the thermoresponsive linear polymers^[26, 27]. The reason was explained tentatively as follows. It was assumed that the optically active linear polymer chains might preferentially form a densely packed structure in water, whereas the optically inactive linear polymer chains only formed a loosely packed structure^[26, 27]. In the thermoresponsive linear polymer system, polymer chain as an entity is responsible for the difference of optically active and optically inactive polymers in thermoresponsive properties. In the dendritic system, linear polymer chains composed of chiral units do not exist, thus the mechanism of packing extent of polymer chains is not applicable. From Scheme 1, it is clear that the chiral Phe units are discretely distributed on the surface of spherical HPEI skeleton. The aggregation of spherical dendritic polymers is normally in the form of packing together many individual polymer spheres through the contact of their surface units^[39]. Thus, the interacting extent of surface groups among dendritic polymers will decide the aggregation extent. D-Phe and L-Phe are complementary units, so the attracting interaction between D-Phe and L-Phe is normally stronger than that among themselves. The optically inactive HPEI-DL-Phe_{0.88} contains both D-Phe and L-Phe units on the surface, and therefore the Phe units of HPEI-DL-Phe_{0.88} might be more preferentially aggregate together than those of the optically active HPEI-D-Phe and HPEI-L-Phe.

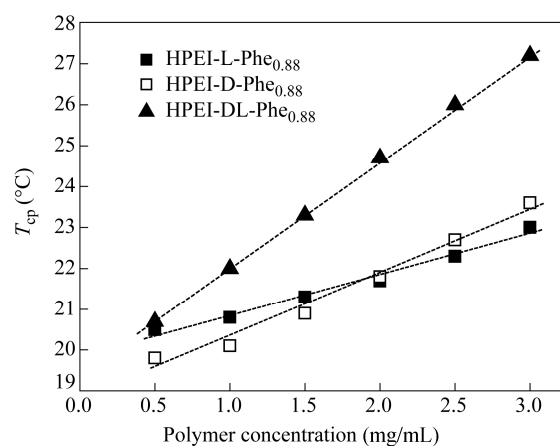


Fig. 4 Comparison of the influence of polymer concentration on T_{cp} of HPEI-Phe_{0.88} with different optical properties in water (0.01 mol/L PBS with pH = 7.0)

CONCLUSIONS

Optically active thermoresponsive hyperbranched polymers, HPEI-D-Phe, HPEI-L-Phe, and their corresponding optically inactive ones, HPEI-DL-Phe, were successfully prepared. All the HPEI-Phe_{0.88} were thermoresponsive in water and those containing higher content of Phe units exhibited lower T_{cp} . The optically inactive thermoresponsive hyperbranched polymers showed a higher T_{cp} than their corresponding optically active ones in a relatively higher polymer concentration. Different from the traditional thermoresponsive polymers, the as-prepared HPEI-Phe_{0.88} exhibited specific thermoresponsive behaviours in water, *i.e.* increasing the polymer concentration led to the increase of T_{cp} in the dilute polymer concentration. Moreover, at the same polymer concentration the hydrophobic groups of the optically inactive HPEI-DL-Phe formed more perfect hydrophobic domain than those of the optically active HPEI-L-Phe and HPEI-D-Phe.

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