

Influence of Aliphatic Amide Terminals on the Thermoresponsive Properties of Hyperbranched Polyethylenimines*

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Abstract Acetamide (C2), propionamide (C3), butyramide (C4), isobutyramide (*i*-C4), isovaleramide (*i*-C5) and trimethylacetamide (*t*-C5) groups each were introduced to the terminals of hyperbranched polyethylenimine (HPEI) through the amidation reaction between HPEI and the corresponding anhydride. Moreover, HPEIs terminated with two kinds of amides were also prepared. The first amide was fixed to be *i*-C4 with 52% degree of amidation (DA), and the second amide varied from C2, C3, C4, *i*-C5 to *t*-C5. All the polymers were characterized by ¹H-NMR. Turbidimetry measurements were performed for these polymers in water at different temperatures. With respect to the polymers bearing only one kind of amide group, except C2, all the other amide groups could render thermoresponsive properties to HPEI. The specific ordering of these amide groups to reduce the cloud point temperature (T_{cp}) was as follows: *i*-C5 > *t*-C5 > C4 > *i*-C4 > C3. Moreover, the more branched *i*-C4 and *t*-C5 were better groups than their less branched isomers C4 and *i*-C5 in the T_{cp} range of 12–51 °C to render the sharper phase transition to the thermoresponsive polymers. As for the polymers bearing two kinds of amide groups, the further introduction of C2, C3, C4, *i*-C5 or *t*-C5 could effectively endow HPEI bearing 52% of *i*-C4 with thermoresponsive properties. The specific ordering of these second amide groups to reduce the T_{cp} was as follows: *i*-C5 > C4 > *i*-C4 > C3 > C2. C4, *i*-C5 and *t*-C5 were all effective second amide groups to prepare the thermoresponsive polymers with sharper phase transition.

Keywords: Aliphatic amide; Hyperbranched; Phase transition; Polyethylenimine; Thermoresponsive polymers.

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 and/or pH, have attracted much interest^[1]. An appealing stimuli-responsive species is thermoresponsive polymers with a lower critical solution temperature (LCST) in aqueous solutions, which show a large decrease in solubility in water above a specific temperature^[2–4].

In 2004 Kono's group reported their pioneering work on the thermoresponsive dendrimers whose LCST could be tuned in a broad range by varying the molecular weight^[5]. Following their pioneering work, more kinds of thermoresponsive dendritic polymers were reported^[6–16]. It was found that the thermoresponsive dendritic polymers as a new member of the family of thermoresponsive polymers exhibited obvious difference in properties compared with the traditional thermoresponsive linear polymers^[5, 16–18]. For instance, the phase transition temperature of the compact hyperbranched polymers exhibited higher sensitivity to ions than that of the traditional thermoresponsive linear polymers^[16, 17].

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Hyperbranched polyethylenimine (HPEI) is a well-known functional polymer and its application fields are very wide. For example, HPEI has been used for a long time not only for various industrial purposes, *e.g.*, as flocculating agents, thickeners and dispersion stabilizers, but also in biomedicine applications, such as gene transfer processes^[19–21]. Endowing HPEI with a further thermoresponsive property will definitely expand its application^[22–25]. Until now, two kinds of thermoresponsive HPEIs with a LCST property have been reported by us. One was the transformation of the reactive amino groups of HPEI into the isobutyramide (IBAm) groups through the amidation reaction between HPEI and isobutyric anhydride^[15, 16]. The other was the amidation between HPEI and the isobutyryl chloride modified valine that contained one secondary amide and two isopropyl units^[26]. In both types of thermoresponsive HPEIs there exist many hydrophilic secondary amides and hydrophobic isopropyl units. Such units are believed to contribute mainly to the thermoresponsive property since they can be found in other well-known thermoresponsive polymers, such as poly(*N*-isopropylacrylamide (PNIPAm)^[27, 28], poly(*N*-vinyl isobutyramide)^[29]. Besides the hydrophobic isopropyl units, we wondered whether other aliphatic units integrated with amide groups could also endow HPEI with thermoresponsive properties. Hence, in this contribution we systematically studied the influence of different aliphatic amide groups on the thermoresponsive properties of HPEIs.

EXPERIMENTAL

Materials

Hyperbranched polyethylenimine (HPEI, Aldrich, $M_n = 1.0 \times 10^4$ g/mol, $M_w/M_n = 2.5$) was dried under vacuum prior to use. Acetic anhydride (95%), propionic anhydride (97%), butyric anhydride (98%), isobutyric anhydride (97%), isovaleric anhydride (97%) and trimethylacetic anhydride (99%) were purchased from Alfa Aesar and used without further purification. Benzoylated cellulose tubing (MWCO 1,200) was purchased from Sigma and used directly. Triethyl amine (A.R., TEA) was dried over CaH_2 and distilled before use. De-ionized water was double-distilled before use. The preparation of HPEI terminated with plenty of IBAm groups (HPEI-IBAm or HPEI-*i*-C4) is similar to that reported previously through the amidation reaction between HPEI and isobutyric anhydride^[17]. The synthetic procedures of HPEIs terminated with plenty of acetamide (C2), propionamide (C3), butyramide (C4), isovaleramide (*i*-C5) and trimethylacetamide (*t*-C5) groups were the same as that of HPEI-*i*-C4, and only the isobutyric anhydride was replaced by the respective acetic anhydride, propionic anhydride, butyric anhydride, isovaleric anhydride and trimethylacetic anhydride.

Nomenclature

C2, C3, C4, *i*-C4, *i*-C5 and *t*-C5 represent acetamide, propionamide, butyramide, isobutyramide, isovaleramide and trimethylacetamide groups, respectively. HPEI- X_y : HPEI- X_y represents HPEI terminated with plenty of amide groups, X represents C2, C3, C4, *i*-C4, *i*-C5 or *t*-C5 and *y* means the degree of amidation (DA) relative to the total reactive primary and secondary amines of HPEI.

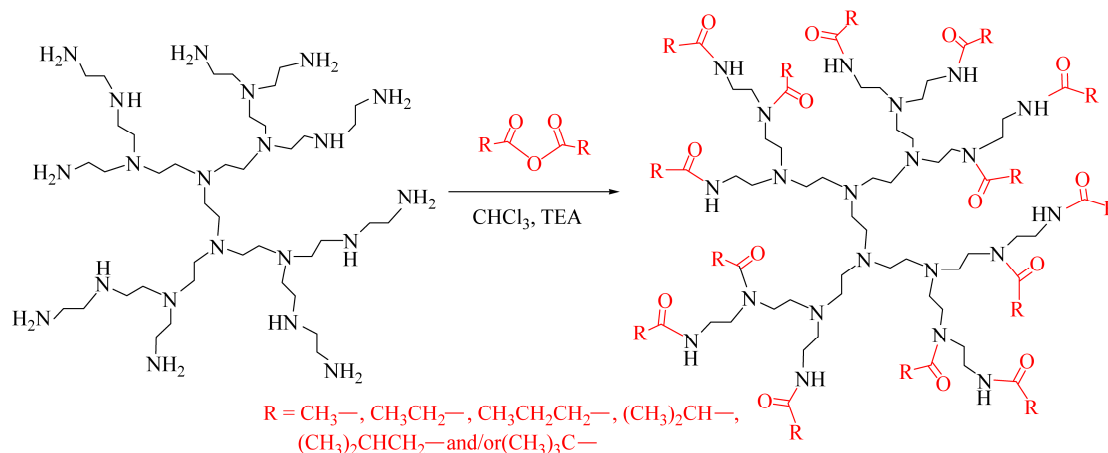
Characterization

¹H-NMR spectra were recorded at 25 °C on a Varian INOVA 500 MHz spectrometer, operated at 500 MHz. Light transmittance of the polymer solution was measured on a temperature-controlled Purkinje General (China) T6 UV/Vis Spectrophotometer at 660 nm, and the heating rate was 0.5 K/2 min. 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. Sharpness of the phase transition ($\Delta T_{1/2}$) is defined as half the values of temperature difference of final break point with initial break point in the transmittance versus temperature curves. The temperature error is ± 0.2 K.

RESULTS AND DISCUSSION

Commercially available HPEI with $M_n = 1 \times 10^4$ g/mol is a hyperbranched polymer that contains primary, secondary and tertiary amine functional groups. Comparing the integrals of carbons adjacent to primary, secondary and tertiary amine groups in the inverted gate ¹³C-NMR spectra^[30], the ratio of primary, secondary and tertiary amines was found to be 33:40:27. In this contribution, the reactive amino groups of HPEI were

amidated with acetic anhydride, propionic anhydride, butyric anhydride, isobutyric anhydride, isovaleric anhydride and/or trimethylacetic anhydride to form the amidated HPEIs (Scheme 1).



Scheme 1 Syntheses of amidated HPEIs with different aliphatic anhydrides

Six series of polymers, including HPEI-C2, HPEI-C3, HPEI-C4, HPEI-*i*-C4, HPEI-*i*-C5 and HPEI-*t*-C5, were prepared and characterized by ¹H-NMR spectra (Fig. 1). In the ¹H-NMR spectra both the HPEI moiety and the aliphatic amides can be assigned clearly. The ethylene protons of HPEI skeleton are in the range of $\delta = 2.2\text{--}3.8$. The signal of methyl protons of the aliphatic amides is separated well from those of the HPEI moiety and other units of the amides. For instance, the methyl protons of C2, C3, C4, *i*-C4, *i*-C5 and *t*-C5 are at around δ of 2.1, 1.1, 0.9, 1.1, 0.9 and 1.2, respectively. According to the integrals of methyl protons and the HPEI moiety, the degree of amidation (DA) relative to the reactive primary and secondary amines of HPEI can be calculated and the data are summarized in Table 1.

Table 1. Structural information of amidated HPEIs and their properties in water^a

No.	Amide	DA ^a (%)	M_n^b (10 ⁴)	General formula	Solubility in water ^c	[polymer] = 20 (mg/mL)			T_{cp} ($\Delta T_{1/2}$) at pH 8.5 ^f (°C)
						pH	T_{cp}^d (°C)	$\Delta T_{1/2}^e$ (K)	
1	C2	100	1.98	HPEI-C2 _{1.0}	s	7.0	—	—	—
2	C3	97	2.26	HPEI-C3 _{0.97}	s	7.0	—	—	56.3(0.5)
3	C3	100	2.30	HPEI-C3 _{1.0}	s	7.0	53.9	0.4	50.1(0.3)
4	C4	69	2.12	HPEI-C4 _{0.69}	s	8.0	31.3	4.6	30.4(4.5)
5	C4	74	2.20	HPEI-C4 _{0.74}	s	8.0	25.7	2.4	24.9(2.4)
6	C4	100	2.63	HPEI-C4 _{1.0}	s	7.0	6.5	0.06	— ^g
7	<i>i</i> -C4	60	1.98	HPEI- <i>i</i> -C4 _{0.60}	s	8.2	—	—	—
8	<i>i</i> -C4	67	2.09	HPEI- <i>i</i> -C4 _{0.67}	s	8.0	40.1	0.6	39.2(0.5)
9	<i>i</i> -C4	79	2.29	HPEI- <i>i</i> -C4 _{0.79}	s	7.5	31.3	0.2	28.1(0.2)
10	<i>i</i> -C4	99	2.61	HPEI- <i>i</i> -C4 _{0.99}	s	7.0	22.9	0.1	14.5(0.1)
11	<i>i</i> -C5	45	1.88	HPEI- <i>i</i> -C5 _{0.45}	s	8.5	20.1	3.9	20.1(3.9)
12	<i>i</i> -C5	58	2.13	HPEI- <i>i</i> -C5 _{0.58}	s	8.2	12.1	2.1	12.1(2.1)
13	<i>i</i> -C5	64	2.25	HPEI- <i>i</i> -C5 _{0.64}	i	—	—	—	—
14	<i>t</i> -C5	38	1.74	HPEI- <i>t</i> -C5 _{0.38}	s	8.5	50.5	0.5	50.5(0.5)
15	<i>t</i> -C5	44	1.86	HPEI- <i>t</i> -C5 _{0.44}	s	8.5	33.8	0.3	33.8(0.3)
16	<i>t</i> -C5	51	2.00	HPEI- <i>t</i> -C5 _{0.51}	s	8.2	21.5	0.3	21.5(0.3)

^a Degree of amidation (DA) is the ratio of amide groups to the reactive amines of HPEI, calculated from the corresponding ¹H-NMR spectrum; ^b Molecular weights were calculated from the ¹H-NMR spectra; ^c s represents soluble in deionized water and *i* represents insoluble in deionized water; ^d T_{cp} means the cloud point temperature that is taken from the intersection of the maximal slope tangent and the initial horizontal tangent in the resulting transmittance versus temperature curve (polymer concentration is 20 mg/mL); ^e $\Delta T_{1/2}$ represents the sharpness of the phase transition and is defined as half the values of temperature difference of final break point with initial break point in the transmittance versus temperature curves; ^f pH was adjusted with NaOH aq; ^g insoluble

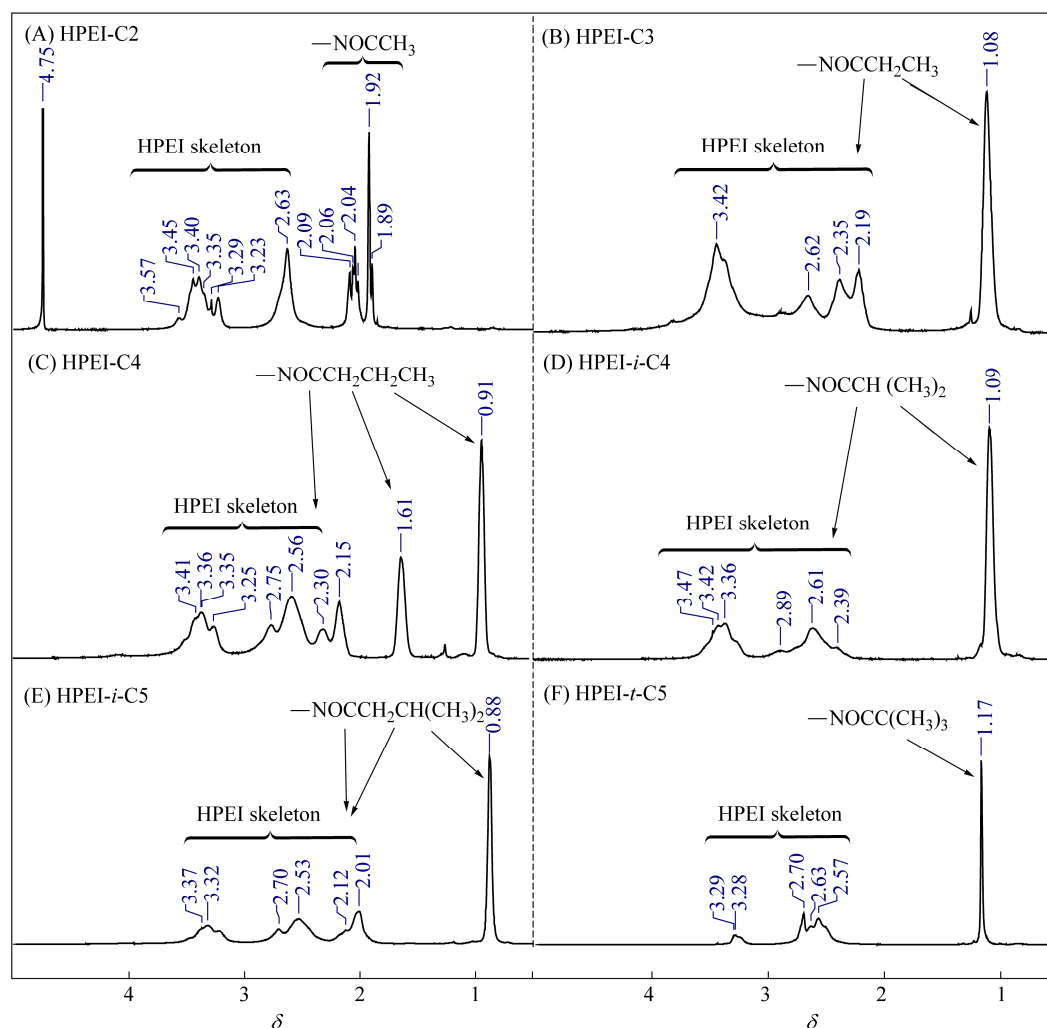


Fig. 1 Typical ^1H -NMR spectra of (A) HPEI-C2, (B) HPEI-C3, (C) HPEI-C4, (D) HPEI-*i*-C4, (E) HPEI-*i*-C5 and (F) HPEI-*t*-C5 in CDCl_3

For the measurement of the properties of these polymers in water, the polymer concentration was fixed to be 20 mg/mL. From Table 1 it can be seen that the pH values of these solutions are a little different, and the polymers with high DA value make pH be close to 7.0, while the polymers with low DA value make pH be close to 8.5. The pH values of all the solutions were adjusted to be 8.5 for the accurate comparison.

For the polymers that are soluble in deionized water, the temperature dependence of the light transmittance of the aqueous solutions of these polymers was studied (Fig. 2). and the data interpreted from Fig. 2 are also summarized in Table 1. HPEI-C2 with 100% DA is water soluble, but is not thermoresponsive in water (Fig. 2a). HPEI-C3 with 100% DA is water soluble and obvious phase transition can be observed for the aqueous solution of this polymer, indicating that HPEI-C3_{1.0} is thermoresponsive (Fig. 2b). Without pH adjustment, the thermoresponsive property of HPEI-C3 disappears when the DA value decreases a little (DA = 97%, pH 7.0). When pH is adjusted from 7.0 to 8.5, an obvious phase transition appears. HPEI-C4 with 100% DA can only dissolve in cold water without pH adjustment (pH 7.0) and an obvious phase transition exists for its aqueous solution, however, it becomes insoluble after the pH adjustment from 7.0 to 8.5 (Fig. 2c). As for HPEI-*i*-C4 with 99% DA, it is always soluble in cold water in the pH range of 7.0–8.5, and obvious phase transitions exist for such aqueous solutions (Fig. 2d). For both HPEI-C4 and HPEI-*i*-C4, the decrease of DA value can effectively increase their phase transition temperature (Figs. 2c and 2d). However, when the DA value is less than a certain

limit, these polymers are not thermoresponsive again. For instance, HPEI-*i*-C4 with DA being no more than 60% is only water-soluble, but not thermoresponsive (Fig. 2d). With respect to HPEI-*i*-C5 and HPEI-*t*-C5, high DA value makes these polymers insoluble in water, but when the DA value is reduced to a certain limit, they become thermoresponsive in water and the phase transition temperature can be enhanced efficiently through the further reduction of DA values (Figs. 2e and 2f). Furthermore, from Fig. 2 and Table 1 it can be concluded that when the DA value is similar, the polymers with longer aliphatic groups have lower T_{cp} (Comparing entries 3 and 6, entries 8 and 13). This is a normal phenomenon since the longer aliphatic group increases the hydrophobicity of the polymer, leading to T_{cp} decrease^[31].

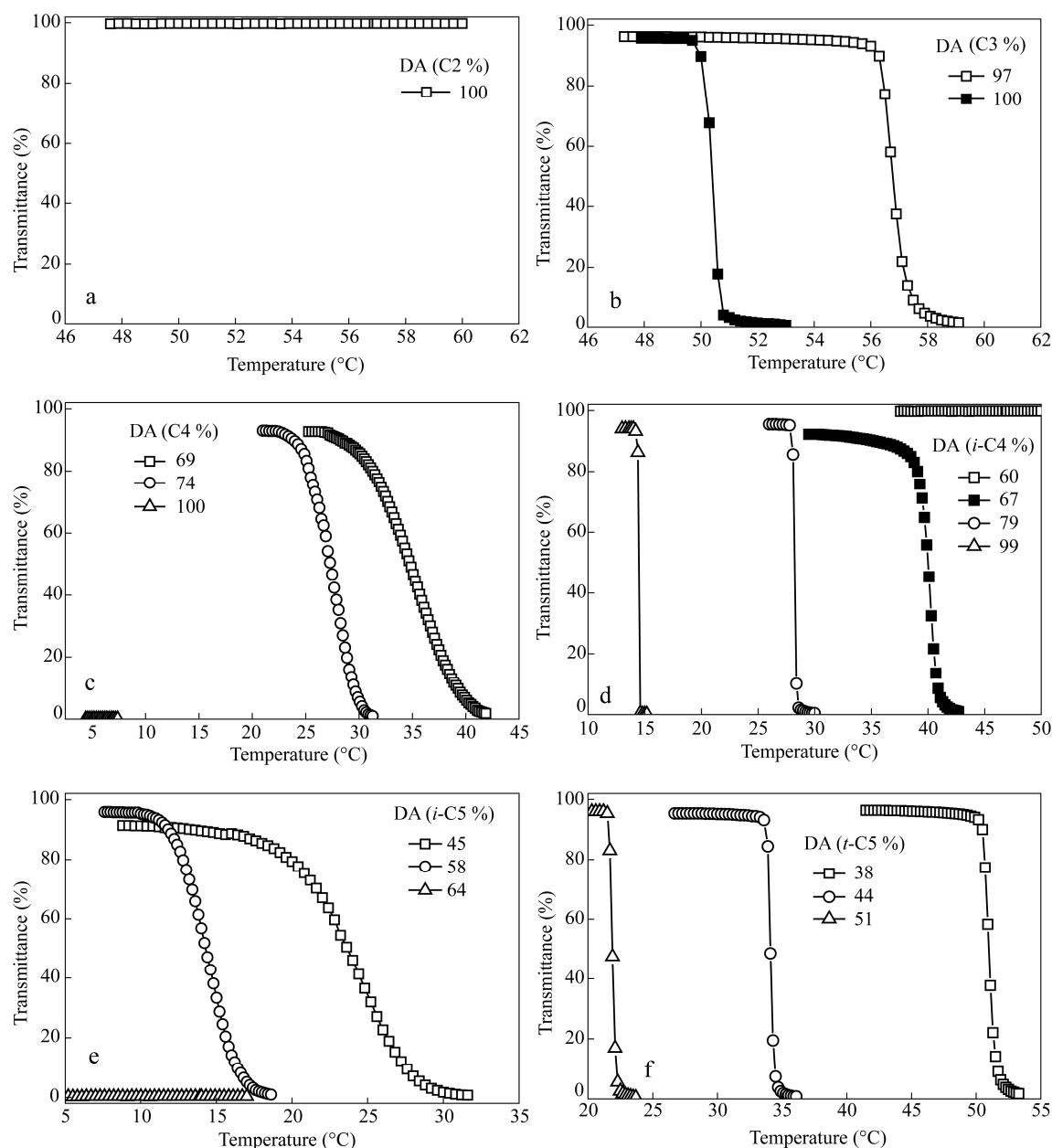


Fig. 2 Typical influence of temperature on the light transmittance of (a) HPEI-C2, (b) HPEI-C3, (c) HPEI-C4, (d) HPEI-*i*-C4, (e) HPEI-*i*-C5 and (f) HPEI-*t*-C5 with different degrees of amidation in deionized water (The concentration of polymers is 20 mg/mL and pH = 8.5.)

C4/*i*-C4 and *i*-C5/*t*-C5 are two series of isomers. Therefore, how the isomer groups influenced the phase transition behavior of the corresponding thermoresponsive polymers was further studied. Figure 3(a) shows that the more branched isomeric groups normally endow a higher T_{cp} to the thermoresponsive polymers of similar DA values. This phenomenon can be explained as follows. Compared with their isomers, *i*-C4 and *t*-C5 bear more methyl and less methylene groups. Methyl unit is relatively less hydrophobic than methylene, therefore *i*-C4 and *t*-C5 are less hydrophobic than their isomers. It is well-known that increasing the hydrophobicity of thermoresponsive polymers decreases the phase transition temperature, whereas increasing the hydrophilicity increases it^[31]. Thus, *i*-C4 and *t*-C5 render a higher T_{cp} to the thermoresponsive polymers than their respective isomers.

Sharp phase transition is a very important property for thermoresponsive polymers employed as smart materials. Until now, many thermoresponsive polymers including dendritic ones have been claimed to have sharp phase transition, however, the data to support that were not given. PNIPAm is an attractive thermoresponsive linear polymer, chiefly because of its well-known abrupt phase-transition nature and LCST close to ambient temperature^[32]. Therefore, we chose PNIPAm as standard to reflect the phase transition property of our polymers. The aqueous solutions of PNIPAm with M_n in the range of 49000–146000 have been measured by microcalorimeter for LCST determination. The width at half-height of microcalorimetric endotherm ($\Delta T_{1/2}$) was used to show the sharpness of phase transition, which were between 0.4 and 0.8 K^[32]. For comparison we defined the sharpness of phase transition of our polymers as half the values of temperature difference between the final and initial break points in the transmittance versus temperature curves. From Fig. 3(b) it can be seen that the more branched *i*-C4 and *t*-C5 are better groups than their less branched isomer C4 and *i*-C5 in the T_{cp} range of 15–51 °C to render the sharper phase transition to the thermoresponsive polymers. For instance, in the T_{cp} range of 12–51 °C the $\Delta T_{1/2}$ values of HPEI-*i*-C4 and HPEI-*t*-C5 are in the range of 0.1–0.5 K, comparable with those of PNIPAm, whereas they are more than 2 K for HPEI-C4 and HPEI-*i*-C5.

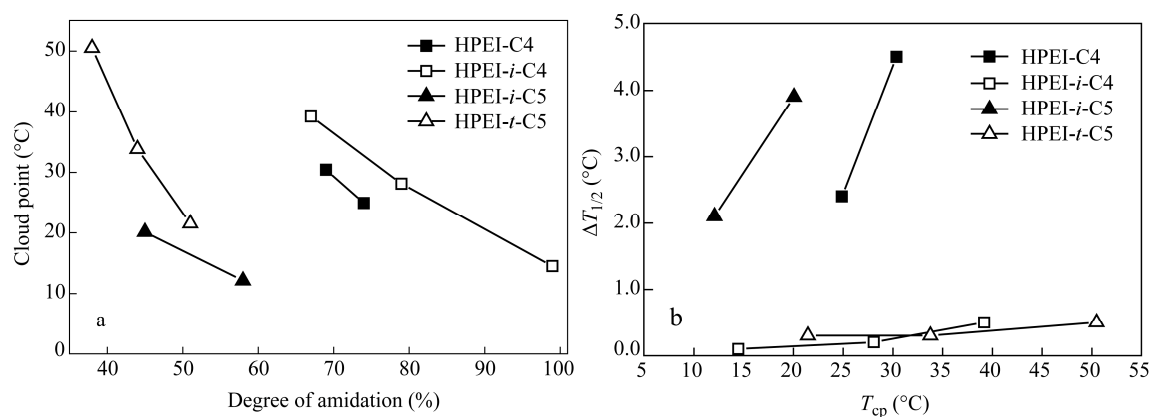


Fig. 3 (a) Influence of degree of amidation on the T_{cp} of thermoresponsive polymers with isomeric groups; (b) influence of isomeric groups on the sharpness of phase transition of the thermoresponsive polymers with different T_{cp} (The concentration of polymers is 20 mg/mL and pH = 8.5.)

We further prepared the thermoresponsive HPEIs concurrently bearing two kinds of aliphatic amide groups and studied their thermoresponsive behavior. For clear comparison, one of the aliphatic amide groups was fixed to be the *i*-C4 group and its DA value was fixed to be 52%. The second amide group employed includes C2, C3, C4, *i*-C5 and *t*-C5. All the samples were characterized by ¹H-NMR (Fig. 4). In the ¹H-NMR spectra both the HPEI moiety and these two aliphatic amide chains can be assigned clearly. The DA value cannot be calculated directly from ¹H-NMR spectra for HPEI-*i*-C4-C3 polymers since the methyl protons of C3 and *i*-C4 are completely overlapped. Therefore, the DA values for HPEI-*i*-C4-C3 polymers are only the theoretical ones

according to the feed number of C3. As for the other polymers, the methyl protons of *i*-C4 can be separated well from those of other amide groups, thus, the DA values can be calculated from the respective ^1H -NMR spectra.

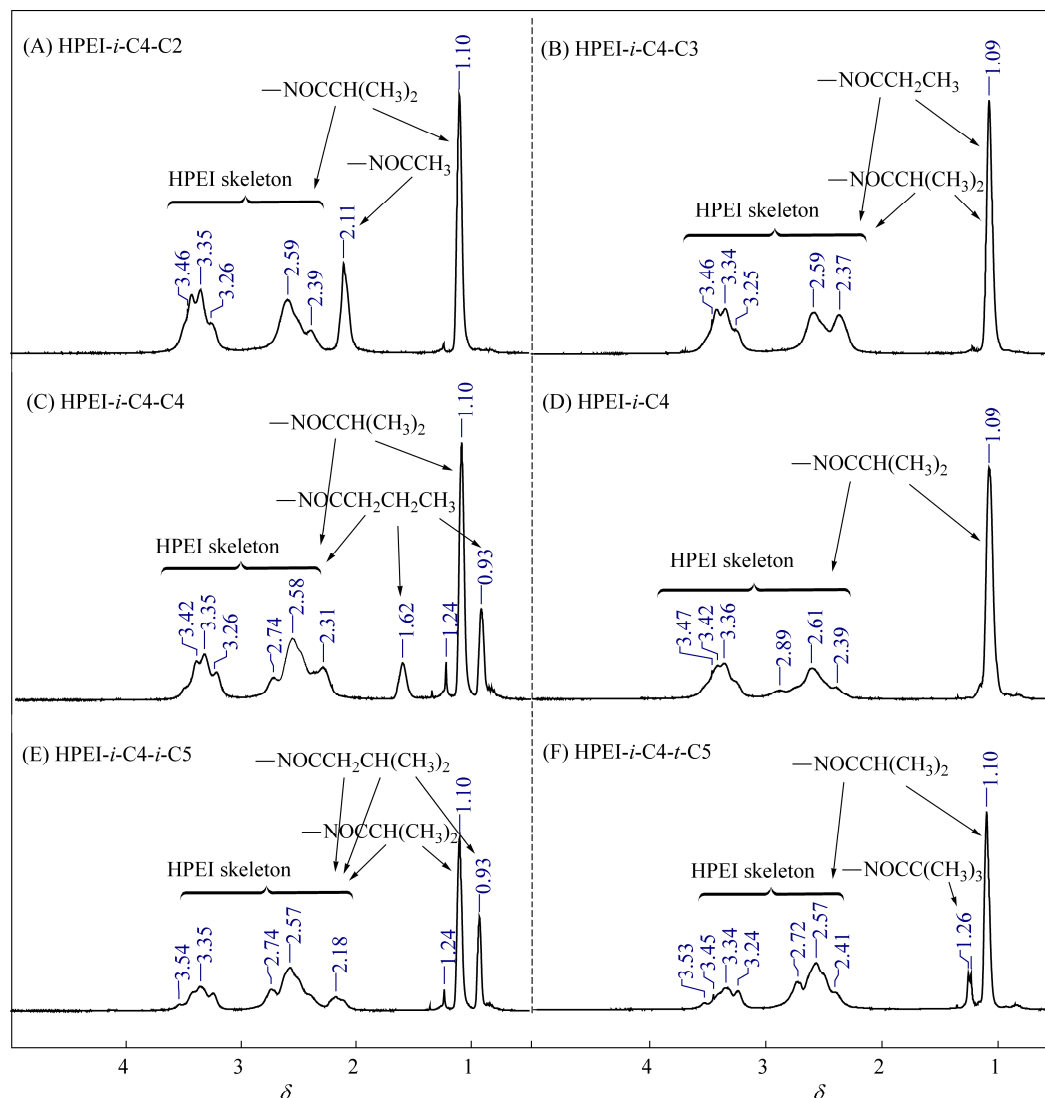


Fig. 4 Typical ^1H -NMR spectra of (A) HPEI-*i*-C4-C2, (B) PEI-*i*-C4-C3, (C) HPEI- *i*-C4-C4, (D) HPEI-*i*-C4, (E) HPEI-*i*-C4-*i*-C5 and (F) HPEI-*i*-C4-*t*-C5 in CDCl_3

The temperature dependence of the light transmittance of the aqueous solutions of such polymers with two kinds of amide groups was studied (Fig. 5). HPEI-*i*-C4_{0.52} in water is not thermoresponsive, however, the further introduction of C2, C3, C4, *i*-C5 or *t*-C5 can effectively endow the polymers with thermoresponsive properties. The more the second amide groups are introduced, the lower the T_{cp} is. From Fig. 6(a) it can be seen that the specific ordering of these amide groups to reduce the T_{cp} is as follows: *i*-C5 > C4 > *i*-C4 > C3 > C2. In this ordering, *t*-C5 is not included since it is difficult to introduce a large amount of such bulky groups to HPEI-*i*-C4_{0.52} under the condition adopted here.

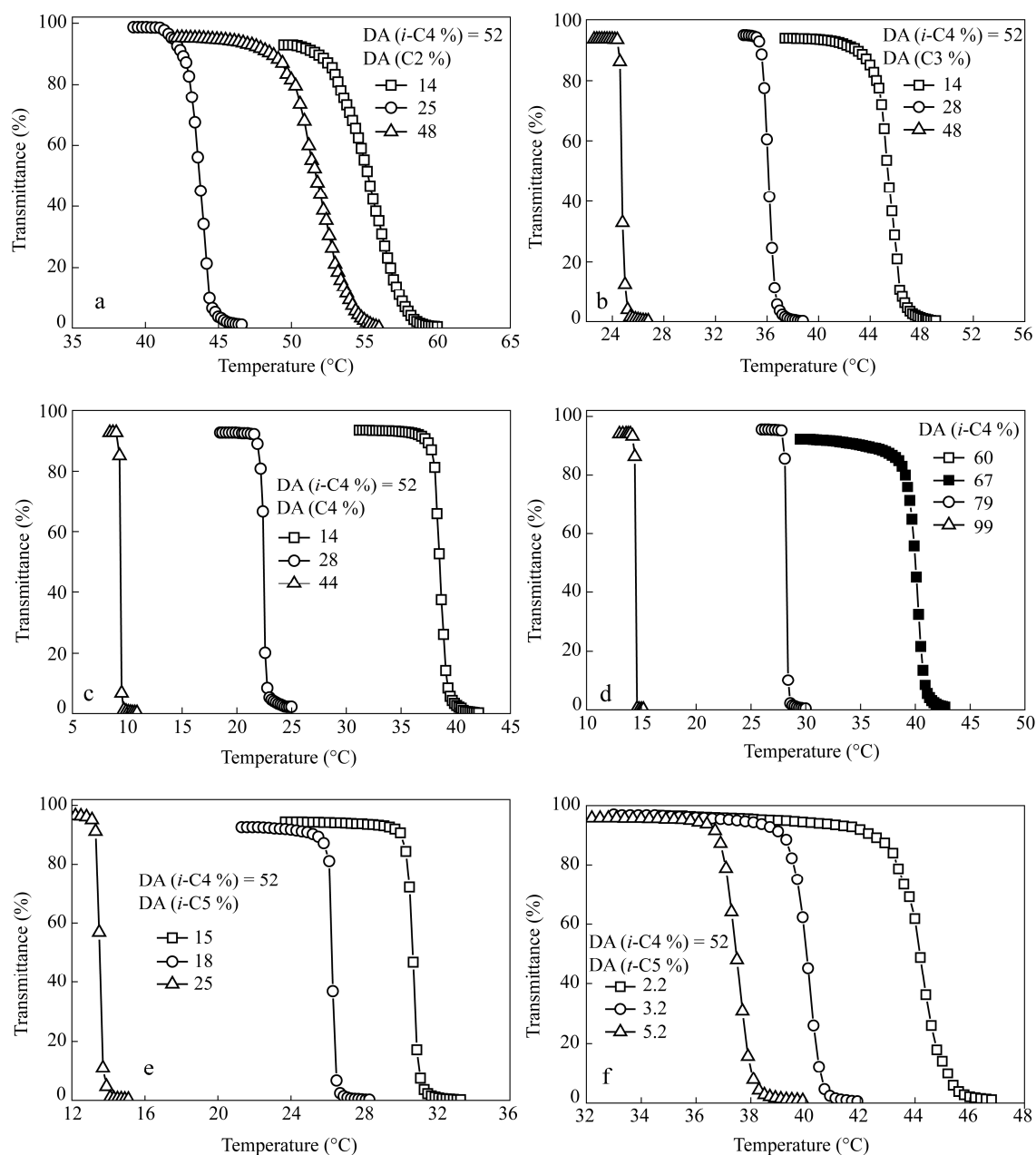


Fig. 5 Typical influence of temperature on the light transmittance of (a) HPEI-*i*-C4-C2, (b) HPEI-*i*-C4-C3, (c) HPEI-*i*-C4-C4, (d) HPEI-*i*-C4, (e) HPEI-*i*-C4-*i*-C5 and (f) HPEI-*i*-C4-*t*-C5 in deionized water (The concentration of polymer is 20 mg/mL and pH = 8.5.)

The sharpness of the phase transition of these polymers with two kinds of amide groups was compared in Fig. 6(b). It is clear that C2 is not an effective group to prepare the thermoresponsive polymers with sharp phase transition. As for C3, its content must reach a certain limit to get the polymers with sharp phase transition. With respect to C4, *i*-C5, and *t*-C5, they all are effective to control the $\Delta T_{1/2}$ value to be no more than 0.8 K. This is different from the polymers with only C4 or *i*-C5 whose $\Delta T_{1/2}$ values are normally more than 2 K.

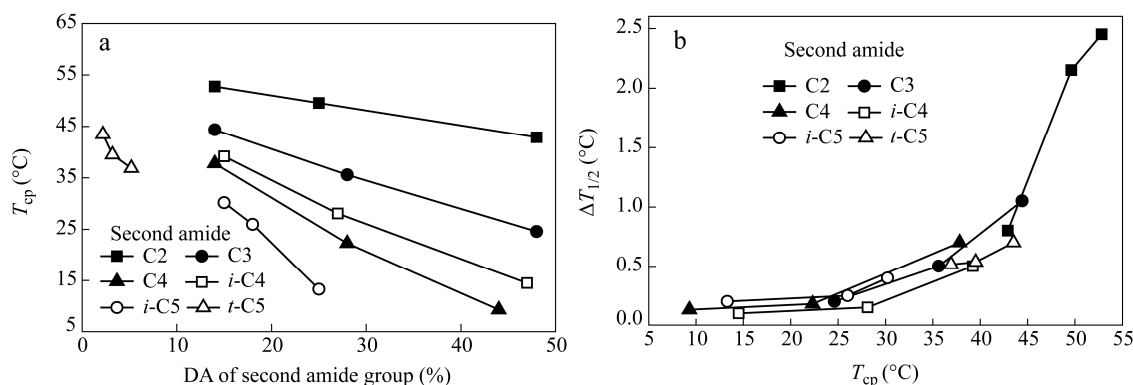


Fig. 6 (a) Influence of degree of amidation of the second amide on the T_{cp} of HPEI with two kinds of amide groups (The DA of *i*-C4 as the first amide unit was fixed to be 52%); (b) influence of the second amide groups on the sharpness of phase transition of the thermoresponsive polymers with different T_{cp} ([polymer] = 20 mg/mL, pH = 8.5.)

CONCLUSIONS

Six series of polymers with only one kind of amide group, including HPEI-C2, HPEI-C3, HPEI-C4, HPEI-*i*-C4, HPEI-*i*-C5 and HPEI-*t*-C5, were prepared through the amidation reaction between HPEI and the respective anhydrides. The properties of the aqueous solutions of these polymers were as follows: (1) HPEI-C2 was water-soluble, but C2 itself could not render HPEI thermoresponsive property; (2) C3 could render HPEI thermoresponsive property, but the DA must be close to 100%; (3) C4, *i*-C4, *i*-C5 and *t*-C5 were all effective units to render HPEI thermoresponsive property and the T_{cp} could be modulated through adjusting the DA value; (4) The more branched isomeric groups normally endowed HPEI a higher T_{cp} ; (5) The specific ordering of these amide groups to render a lower T_{cp} value to HPEI was as follows: *i*-C5 > *t*-C5 > C4 > *i*-C4 > C3; (6) The more branched *i*-C4 and *t*-C5 were better groups than their less branched isomer C4 and *i*-C5 in the T_{cp} range of 12–51 °C to render the sharper phase transition to the thermoresponsive polymers.

Five series of polymers with two kinds of amide groups were prepared through the amidation reaction between HPEI and two kinds of anhydrides. The first amide was fixed to be *i*-C4 and the second amide varied from C2, C3, C4, *i*-C5 to *t*-C5. The properties of the aqueous solutions of these polymers were as follows: (1) When the DA value of *i*-C4 was fixed to be 52%, the further introduction of C2, C3, C4, *i*-C5 or *t*-C5 could effectively endow HPEI-*i*-C4_{0.52} with thermoresponsive properties; (2) The more the second amide groups were introduced, the lower the T_{cp} was; (3) The specific ordering of these second amide groups to reduce the T_{cp} is as follows: *i*-C5 > C4 > *i*-C4 > C3 > C2; (4) C2 was not an effective second amide group to prepare the thermoresponsive polymers with sharp phase transition; (5) The content of C3 as the second amide group should reach a certain limit to get the thermoresponsive polymers with sharp phase transition; (6) C4, *i*-C5 and *t*-C5 were all effective second amide groups to control the $\Delta T_{1/2}$ value to be no more than 0.8 K.

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