Phase Transition and Conformational Variation of N-Alkylated Branched Poly(ethyleneimine) Comblike Polymer

Haifeng Shi,[†,§] Ying Zhao,[†] Xiuqin Zhang,[†] Shichun Jiang,[‡] Dujin Wang,[*,†] Charles C. Han,[†] and Duanfu Xu[†]

Key Laboratory of Engineering Plastics, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China, State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China, and Graduate School of Chinese Academy of Sciences, Beijing 100080, China

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ABSTRACT: A series of branched poly(ethyleneimine) (PEI) derived polymers with different lengths of *n*-alkyl side chains, denoted as PEI(*n*)Cs ($n = 12, 14, 16, 18, 20$, number of carbon atoms in alkyl side group), have been prepared by a N-alkylation method, and systematically characterized by differential scanning calorimertry (DSC) and wide-angle X-ray diffraction (WAXD) as well as Fourier transform infrared spectroscopy (FTIR). The side chains grafted on these comblike polymers are long enough to form crystalline phase composed of paraffin-like crystallites. The crystallization of the side chains forces the branched poly(ethyleneimine) molecules to pack into layered structure, between which the crystallites are located. The melting temperatures of the side chain crystallites increase from −12.36 to +51.49 °C with increasing the length of the side chains from $n = 12$ to $n = 20$, which are a little bit lower than the corresponding pristine *n*-alkanes. PEI18C was taken as an example in this work for the investigation of phase transition and conformational variation of the side chains with temperature changing. With temperature increasing, the crystalline phase of the side chains undergoes a phase transition process from orthorhombic to hexagonal form and then from hexagonal to melt state. Similarly, increasing temperature leads to the regular trans sequences of the orthorhombic phase transforming to conformationally disordered trans sequences of the hexagonal phase and then to the gauche conformational state (melt state) at higher temperature. The above-described experimental phenomena for both crystalline transition and conformational structure variation are reversible as temperature decreases. Combining the transformations of the crystalline phase and the conformational structure, it is confirmed that hexagonal phase exists as an intermediate phase in the process of temperature variation.

Introduction

Comblike polymers, possessing *n*-alkyl side chains, occupy a special position among numerous branched and linear polymers. They differ from the ordinary branched polymers by number and density of the side chain, which results in the appearance of some new properties. Synthesis, structure, and properties of comblike polymers have been extensively researched in the passed several decades, and many original investigations and reviews have been published.[1−35] The first comblike polymer was synthesized by Rehberg and Fisher through polymerizing *n*-alkyl acrylates,[2] and since then this type of polymer has been a permanent subject for synthesis chemistry and physical characterization as well as materials modification and processing. Comblike polymers are generally divided into two sorts, considering the rigidity of the backbones: rigid-rod main-chain polymers and flexible main-chain polymers, both of which are grafted with long flexible side chains.

The thermotropic phase behavior, layered structure, and crystalline phases developing from the layered mesophases are the characteristic structures for comblike polymers, which have great influence on the performances of the polymeric backbones.[36] Interestingly, the crystallization behavior and conformational ordering of the side chains can modify not only the rigidity but also the solubility of backbones by acting much in a way of a "bound solvent", which may increase the entropy of dissolution and by screening the interaction between main chains.[25] More specifically, the alkyl side chains, which have a profound influence on the microstructure of the comblike polymer, introduce some unique properties such as solvatochromic behavior and reversible thermochromic transition between low and high-temperature solid-state phases.[37] Jordan studied the thermal behavior of a series of comblike polymers, such as poly(*n*-alkyl acrylates),[3,4] poly(*N*-*n*-alkylacrylamide),[5,6] poly(*N*-*n*-alkylmaleimide),[7−9] and poly(vinyl ester)[10,11] with unbranched alkyl side chains containing 12−22 carbon atoms by using DSC method. The authors thought that only the outer alkyl side chains, exceeding 8−10 methylene groups, are able to crystallize. Moreover, WAXD and ^{13}C NMR investigations on poly(*n*-alkyl methacrylates)[12,13] and poly(*n*-alkyl itaconate)s[14,15] also show that the alkyl side chain are able to crystallize in hexagonal lattice when its length reaches 12. The investigation results for aromatic polyamides,[16−24] polyanilines[25] and polythiophenes,[26−28] and N-alkylated poly(*p*-benzamide)[29] as well as poly(γ-alkyl-α,L-glutamate)s,[30−35] however, suggested that only when the number of carbon atoms in the side chains is 12 or higher can the side chain crystallization behavior be observed.

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[*] To whom correspondence should be addressed. E-mail: djwang@iccas.ac.cn.

[†] Institute of Chemistry, Chinese Academy of Sciences.

[‡] Changchun Institute of Applied Chemistry, Chinese Academy of Sciences.

[§] Graduate School of Chinese Academy of Sciences.

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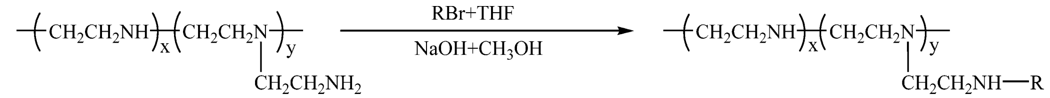
Scheme 1. Synthesis of N-Alkylated PEI Comblike Polymers[a]



$$-\!\left(\mathrm{CH_2CH_2NH}\right)_x\!\left(\mathrm{CH_2CH_2}\underset{\mathrm{CH_2CH_2NH_2}}{\underset{|}{\mathrm{N}}}\right)_y\!- \xrightarrow[\mathrm{NaOH+CH_3OH}]{\mathrm{RBr+THF}} -\!\left(\mathrm{CH_2CH_2NH}\right)_x\!\left(\mathrm{CH_2CH_2}\underset{\mathrm{CH_2CH_2NH{-}R}}{\underset{|}{\mathrm{N}}}\right)_y\!-$$

[a] R = $-C_{12}H_{25}$, $-C_{14}H_{29}$, $-C_{16}H_{33}$, $-C_{18}H_{37}$, or $-C_{20}H_{41}$.

Table 1. Degree of Alkylation Determined by Elemental Analysis of N-Alkylated Poly(ethylenimine)

polymer	substitution groups	degree of alkylation determined by nitrogen content/%
PEI12C	*n*-dodecyl	52.9
PEI14C	*n*-tetradecyl	54.6
PEI16C	*n*-hexadecyl	43.0
PEI18C	*n*-octadecyl	44.2
PEI20C	*n*-eisocyl	47.0

Poly(ethyleneimine) (PEI) is a highly branched, water-soluble polymer, which is widely used in paper industry. On the basis of the chemical reactivity of the amino groups on backbones, a number of supramolecular complexes have been prepared through the interaction of PEI molecules with metal ions,[38] anionic polyelectrolytes,[39−41] and surfactants.[42−44] In our previous work, we have reported the lamellar structure and crystalline transition of PEI/octadecanoic acid complexes formed through interactions of proton transferring and hydrogen bonding.[45−47] However, to the best of our knowledge, PEI based complexes with side alkyl chains, which are synthesized via covalent bonding, so far have not been investigated from the viewpoint of aggregation state and side chain crystallization. These complexes are believed to have different self-assembled structures and crystallization behaviors, compared with those for the complexes formed through noncovalent interactions, such as electrostatic atracting and hydrogen bonding.

It is therefore the main objective of this work to synthesize and characterize a series of comblike polymers of PEI with different length of *n*-alkyl side chains (PEI(*n*)Cs, $n = 12, 14, 16, 18, 20$, number of carbon atoms in the side alkyl group). The complexes were prepared by a N-alkylation method, which has been reported by Nöding for the synthesis of amphiphilic poly(ethyleneimine) with long-chain alkyl bromides.[48] The structure and properties of the obtained derivatives were examined by differential scanning calorimertry (DSC), wide-angle X-ray diffraction (WAXD), and Fourier transform infrared spectroscopy (FTIR). In particular, we have tried to understand what kind of ordered structure exists and what effect the length of the side chain alternation has in the PEI(*n*)Cs comblike polymers. Molecular packing mode and phase transition behavior in the series of PEI(*n*)Cs are also discussed.

Experimental Section

1. Materials. Poly(ethyleneimine) (average $M_w = 25\,000$) was purchased from Aldrich and was used as received. The ratio of primary, secondary and tertiary amino groups was 1:2:1.[49] A series of *n*-alkyl bromides were reagent grades obtained from ACROS and were used as received.

2. Preparation of *N*-Alkylated PEI. A 1 g (0.023 mol EI unit) sample of branched poly(ethyleneimine) and an equivalent amount of *n*-alkyl bromide were heated under reflux in 100 mL of tetrahydrofuran for 48 h. An equivalent amount of sodium hydroxide, dissolved in methanol, was added, and the solution was heated under reflux for another 24 h. After cooling to room temperature, NaBr was filtered off, and the solvent was removed. The product was rinsed alternatively with deionized water and acetone three times, and then dried in a vacuum. The reaction equation is shown in Scheme 1.

3. Characterization. Nuclear Magnetic Resonance Spectroscopy (NMR). A general Bruker DMX-300 Fourier transform nuclear magnetic resonance spectrometer (FT-NMR) operating at 300 MHz was used to determine the molecular structures of PEI(*n*)Cs in $CDCl_3$.

Differential Scanning Calorimetry (DSC). A Mettler differential scanning calorimeter (model DSC822), calibrated with indium, was used to study the thermal behavior of PEI(*n*)Cs. Specimens of 3−5 mg were encapsulated in aluminum pans and heated at a rate of 10 °C /min from −60 to +100 °C, and kept at 100 °C for 10 min; they were subsequently cooled to −60 °C at a rate of 10 °C /min and kept at −60 °C for 10 min; and the samples were heated again at a rate of 10 °C /min from −60 °C to +100 °C. The DSC thermograms were recorded.

Wide-Angle X-ray Diffraction (WAXD). Wide-angle X-ray measurements of different PEI(*n*)Cs samples were performed on a Rigaku D/max-2500 X-ray diffractometer at room temperature (ca. 25 °C). The power for the X-ray diffraction is 200 mA, 40 kV. The X-ray source is an 18 kW rotating anode X-ray generator equipped with a Cu target. The incident X-ray beam was monochromated by a pyrolytic graphite and the data were collected from $2\theta = 1$ to 40°. The intensity profile was output as plot of the scattering intensity (I) vs the diffraction angle (2θ). The temperature varying wide-angle X-ray diffraction measurements were performed over the temperature range of 30−160 °C, using copper Kα radiation of wavelength 1.542 Å.

Temperature-Dependent Fourier Transform Infrared Spectroscopy (FTIR). The PEI(*n*)Cs were mixed with KBr powders, and the mixture was then pressed into a thin pellet. The FTIR measurements were performed on a Bruker EQUINOX 55 spectrometer equipped with a temperature-variable cell and the obtained spectra were processed with a Bruker OPUS program. The cell was kept in a vacuum, and liquid nitrogen was used as coolant. A resolution of 2 cm^{-1} was chosen, and 64 scans were accumulated. Infrared spectra were recorded as temperatures ranging between −100 and +100 °C during heating or cooling process. At each temperature point, the samples were equilibrated for 5−8 min before measurements.

Results and Discussion

Composition Measurement of PEI(*n*)Cs. The degree of alkylation was determined by elemental analysis and is defined as the percentage of alkylated monomer units relative to all monomer units (see Scheme 1). The calculation process of alkylation degree was done according to Nöding,[48] and the results are listed in Table 1. For structural confirmation of the alkyl side chains, PEI18C was given as an example. Parts a and b of Figure 1 show the ^{13}C NMR spectra of PEI and PEI18C in $CDCl_3$, respectively. The peaks at 13.95 and 22.54 ppm are characteristic signals of carbon atoms of CH_3 and terminal CH_2 of alkyl side chain in PEI18C, respectively. Peaks for the inner methylene carbons of side alkyl chains fall in the range of 25.93−29.59 ppm. The peak of methylene of alkyl side chain connected with the N atom falls in the range of 42−55 ppm.

Thermal Behavior of PEI(*n*)Cs. The thermal properties of PEI(*n*)Cs were investigated by differential scanning calorimetry. It was found that none of the derivatives shows a glass transition in the temperature range from −60 to +100 °C, probably due to the addition

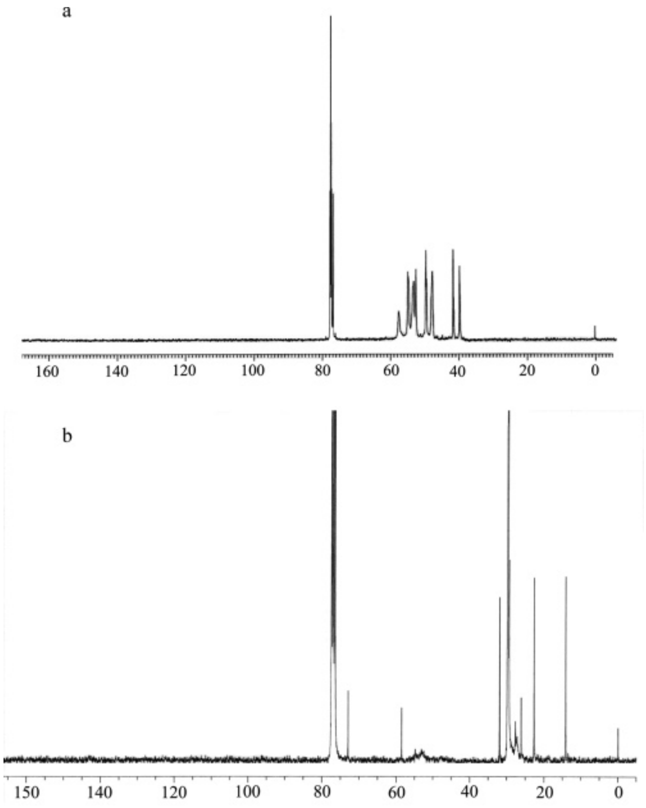


Figure 1. ^{13}C NMR spectra of PEI (a) and PEI18C (b) in $CDCl_3$.

of alkyl side chains on PEI backbones (Figure 2). Endothermic or exothermic transitions were found for all the PEI(*n*)Cs comblike polymers, and the transitions gradually increase from −12.36 (PEI12C) to +51.49 °C (PEI20C) (Table 2). We assign these transitions to the melting points of the crystallized side chains grafted on PEI backbones. Similar results have been obtained for some other comblike polymers with long alkyl side chains, such as poly(*n*-alkyl acrylate),[3,4] poly(*n*-alkyl methacrylate),[12,13] N-alkylated polybenzamide,[29] N-alkylated copolyamides,[50] poly[*N*-(10-*n*-alkyloxycarbonyl-*n*-alkyl)] maleimides,[51] and poly(*n*-alkyl itaconate).[14,15] Figure 3 shows the melting temperatures, T_m, of PEI(*n*)Cs and the corresponding *n*-alkanes. It was observed that increasing the alkyl chain length leads to higher melting points for both PEI(*n*)Cs comblike polymers and *n*-alkanes, however, the T_m values of PEI(*n*)Cs are a little bit higher than those of *n*-alkanes, and the difference is enhanced by increasing the alkyl chain length. For example, the T_m value of the PEI12C/PEI20C is 0.36/15.49 °C higher than those of n-$C_{12}H_{25}$ and n-$C_{20}H_{41}$, respectively. By DSC results, we can come to a temporary conclusion that the packing mode of the alkyl side chains in PEI(*n*)Cs is different from that of the corresponding *n*-alkanes.

To estimate the degree of crystallinity of alkyl side chains in PEI(*n*)Cs comblike polymers, the melt enthalpies (ΔH_m) were determined. Because of the same history of thermal treatment for all the samples in DSC measurement, the second heating run was used for evaluation and comparison of the crystallinity of alkyl side chains in the PEI(*n*)Cs samples. As expected, it was found that the melt enthalpies increase linearly (Figure 4) with the number of carbon atoms of the alkyl side chains, which is in good agreement with the experimental results of the melting temperatures of PEI(*n*)Cs (Figure 3). The quantities of the melting points (T_m), crystallization temperature (T_c), melt enthalpies (ΔH_m), melt entropies (ΔS_m), percent crystallinity (X_c) and number of crystalline CH_2 groups (N_c, to be described later on) in the side chains are listed in Table 2. The linearity between ΔH_m and carbon numbers of alkyl side chains is usually observed for flexible main-chain comblike polymers and is represented by the following equation:[52]

$$\Delta H_m = nk + \Delta H_{m,e} \tag{1}$$

where k is the contribution of each added methylene group to the enthalpy and $\Delta H_{m,e}$ is a constant reflecting the contribution to the enthalpy due to the chain end. The value of k, evaluated from the solid line in Figure 4, is 2.5 ± 0.1 kJ/mol of methylene group, and $\Delta H_{m,e}$ is −15.6 ± 2.8 kJ/mol. In addition, it is well-known that the average enthalpy gain per mole of CH_2 is sensitive to the type of crystal lattice adopted by the polymethylenic chain. For the crystalline transition of *n*-alkanes, the k values are around 3.99 or 4.2 kJ/mol·CH_2 from rhombic or triclinic to liquid state, whereas the k values are on the order of 3.07 kJ/mol·CH_2 from hexagonal to liquid state.[50] The resulting k values for PEI(*n*)Cs in the present work are smaller than that of the corresponding *n*-alkanes, indicating that the alkyl side chains form less-dense subcells in the partially crystalline regions of PEI(*n*)Cs comblike polymers. Moreover, because the k value of 2.5 ± 0.1 kJ/mol·CH_2 is close to 3.07 kJ/mol·CH_2, it can be postulated that the alkyl side

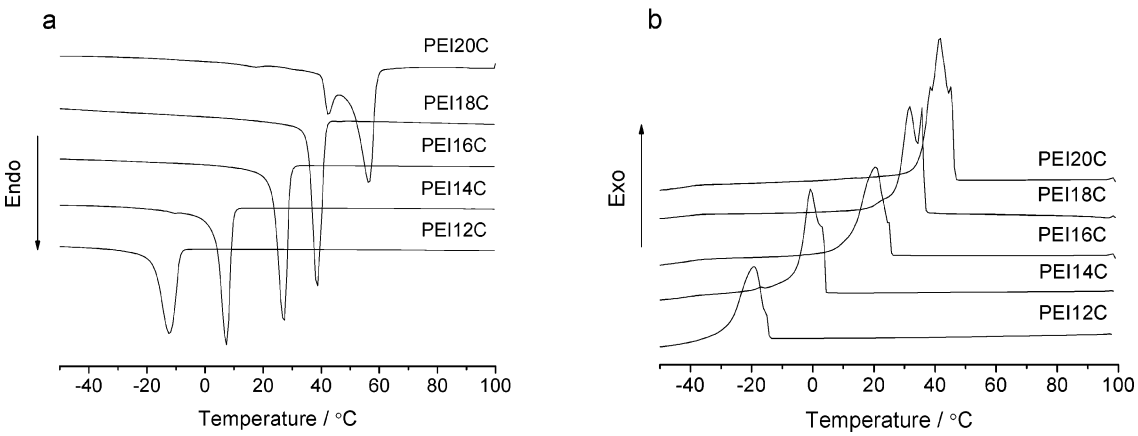


Figure 2. DSC thermograms of PEI(*n*)Cs: (a) heating process; (b) cooling process.

Table 2. Calorimetric Data for N-Alkylated PEI Comblike Polymers: T_m, Melting Points; T_c, Crystallization Temperature; ΔH_m, Melt Enthalpies; ΔS_m, Melt Entropies; X_c Percent Crystallinity; N_c, Number of Crystalline CH_2 Groups in the Side Chains

polymer	T_m/°C	T_c/°C	ΔH_m/(kJ/mol)	ΔS_m/(kJ/mol·K)	X_c/%	N_c
PEI12C	−12.36	−19.19	15.05	0.058	40	6.02
PEI14C	7.37	−0.65	20.68	0.074	48.5	8.27
PEI16C	27.23	20.64	24.37	0.081	51.2	9.75
PEI18C	38.6	31.6	28.93	0.093	55	11.57
PEI20C	15.75/51.49	41.51	36.37	0.11	63.2	14.55

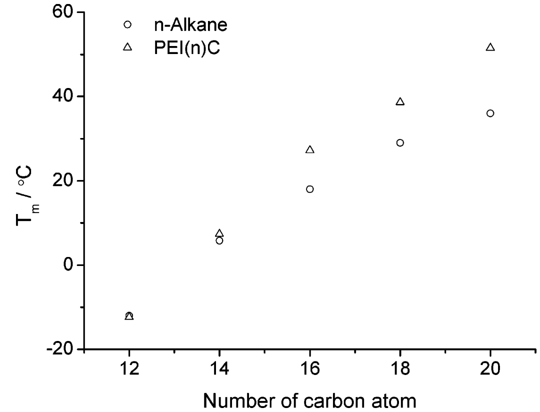


Figure 3. Comparison of the melting points of PEI(n)Cs and the corresponding pristine n-alkanes.

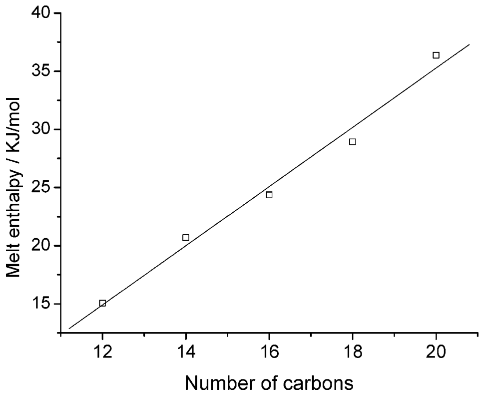


Figure 4. Melt enthalpy of PEI(n)Cs vs the number of carbons of the alkyl side chains. The "□" values are experimental data, and the solid line is a linear fit with a slope of 2.5 kJ/mol of methylene groups.

chain might be packed into a "hexagonal"-like crystal structure, which is similar to that of conventional comblike polymer, such as poly(n-alkyl acrylate), poly(n-alkyl methacrylate), N-alkylated copolyamides, poly[N-(10-n-alkyloxycarbonyl-n-alkyl)] maleimides, and poly(n-alkyl itaconate). This conclusion will be further confirmed by X-ray diffraction data later on.

In addition, the calculation of the entropic change (ΔS_m) during the melting process has been performed based on the presumption that the crystals are at the thermodynamic equilibrium:

$$\Delta S_m = \Delta H_m / T_m \tag{2}$$

Table 2 shows the values of ΔS_m increases from 0.058 (PEI12C) to 0.11 (PEI20C). The result further proves that the ordered degree of molecular conformation and packing improves with increasing the length of side alkyl chains.

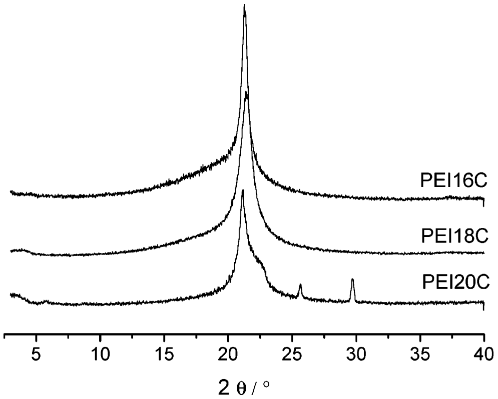


Figure 5. X-ray diffraction of N-alkylated PEI comblike polymers.

According to Jordan,[3] the numbers of crystalline CH_2 groups (N_c) in a side chain and the crystallinity (X_c) can be calculated using the following equation:

$$N_c = \Delta H_m / k \tag{3}$$

$$X_c = N_c \times 14.026 / M_{\text{unit}} \tag{4}$$

Table 2 also shows that N_c increases from 6.02 (PEI12C) to 14.55 (PEI20C) and the X_c increases from 40 (PEI12C) to 63.2% (PEI20C). From this table, it can be concluded that the tails of the alkyl side chain extending beyond certain limit can participate in the crystallization. The observed result is in disagreement with the work of Watanabe,[53] who found that the first 10 methylene groups are in a disordered or liquidlike state. The possible reason is that the much more flexible main chain of the branched PEI molecules makes the side chain move more easily, thus resulting in the crystallizable carbon atoms increasing. Therefore, it can be concluded that the flexibly branched PEI main chain tends to adapt itself by allowing the alkyl side chains to be easily packed into crystal lattice.

WAXD Studies of PEI(n)Cs. Figure 5 shows the WAXD profiles of the as-made powder N-alkylated PEI derivatives at room temperature. Because PEI12C and PEI14C are in the liquid state at room temperature, WAXD analysis was not carried out on these two samples. Thus, only the diffraction results of PEI16C, PEI18C, and PEI20C will be discussed in the following paragraph.

As shown in Figure 5, the three PEI(n)Cs derivatives exhibit the same reflection peak at $2\theta \leq 21.4°$, corresponding to a spacing of 4.2 Å. This indicates that the alkyl side chains in these polymers crystallize in hexagonal lattice in analogy with conventional comblike polymers, such as poly(n-alkyl acrylate),[3,4] poly(n-alkyl methacrylate),[12,13] and poly(n-alkyl itaconate).[14,15] Besides the typical diffraction peak of hexagonal crystal, two weak diffraction peaks at $2\theta = 26.2°$ ($d = 3.4$ Å) and $2\theta = 29.8°$ ($d = 3.0$ Å) were also detected for

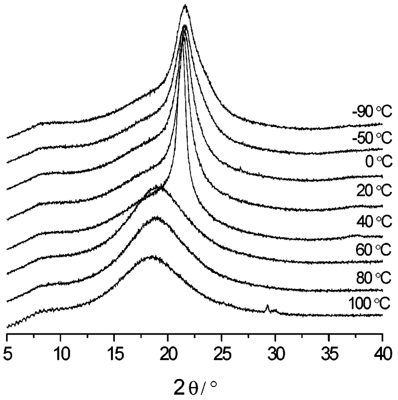


Figure 6. X-ray diffraction of PEI18C taken at different temperatures.

PEI20C, which up to date are not well understood. They might be caused by the layered structure formed by PEI20C at room temperature.[54] It is worthwhile to note that a shoulder at $2\theta = 23.4°$, corresponding to a spacing of 3.8 Å, was obviously observed at the right side of $2\theta \leq 21.4°$. The presence of such a shoulder indicates that the alkyl side chains also pack into an orthorhombic lattice.[55,56]

To gain insight into the crystallization behavior of the synthesized PEI(n)Cs comblike polymers, the X-ray diffractograms of PEI18C were recorded as temperature increasing from −90 to +100 °C (Figure 6). The curve-fitting result for the diffractogram at −90 °C (not shown here) gave a shoulder at $2\theta = 23.4°$ ($d = 3.8$ Å) and a very strong peak at $2\theta = 21.4°$ ($d = 4.2$ Å), characteristic peaks for orthorhombic structure. With temperature increasing, the shoulder gradually disappears ($T > 20$ °C) and the sharp peak at $2\theta = 21.4°$ changes into a broad peak at smaller angle ($2\theta = 19.3°$, $d = 4.6$ Å), indicating that the melting of the polymethylene side chains takes place during the heating run. The present result is similar to that of poly(β-L-aspartate) containing linear alkyl side chains,[57] for which the disappearance of the sharp diffraction peak in the wide-angle region clearly corresponds to the fusion of the paraffinic crystallites. Such a transformation from orthorhombic to hexagonal to melt state was also confirmed by FTIR spectroscopy, which will be presented below.

FTIR Investigations on Conformational and Crystalline Transitions of PEI(*n*)Cs. Infrared spectroscopy has been proved to be a powerful tool for the study of structural variation of polymers, and in particular to be suitable for evaluating the conformational disorder and packing mode of polymethylene chains. Therefore, to investigate the conformational and phase transition behavior of the crystallized alkyl side chains in PEI(n)Cs, a temperature-dependent FTIR technique was used in this work. The IR spectrum of PEI18C with temperature changing is given as an example for the analysis of the crystallization behavior and conformational transition of PEI(n)Cs comblike polymers.

(a) CH_2 Bending Vibrational Region. Figure 7 shows the bending vibrational bands of FTIR spectra for PEI18C as a function of temperature. As shown in Figure 7a, with temperature increasing, the intensity of orthorhombic crystalline band (1471 cm^{-1}) decreases and the 1463 cm^{-1} peak shifts to higher frequency; as temperature exceeds 20 °C, a new band (1466 cm^{-1}) representing the hexagonal phase was observed, accompanied by the disappearing of the orthorhombic bands (1471 and 1463 cm^{-1}). This means that the orthorhombic crystal lattice is transformed to a hexagonal crystal lattice, or in other words, what happens is that there is a transformation from conformationally ordered chains (all-trans, planar) to conformationally disordered chains (intermediate phase between ordered and melt state). The behavior of the infrared bands of PEI18C in this region is similar to that observed in the orthorhombic-to-hexagonal phase transition of $C_{19}H_{40}$,[58] $C_{29}H_{60}$,[59,60] and constrained PE.[61,62] With temperature further increasing from 20 to 100 °C, the intensity of the trans conformational band at 1466 cm^{-1} gradually decreases, while that of the gauche conformational band at 1457 cm^{-1} increases accordingly. The trans−gauche conformational change is easily to be understood. The intensity of 1466 cm^{-1}, characteristic of conformationally disordered chains, first increases in the temperature region of orthorhombic-to-hexagonal phase transition and then decreases down to that of the melt. As reported by Wunderlich,[63−65] the hexagonal phase may be considered to consist of parallel packing of the conformationlly disordered molecular chains which are constructed by the randomly arrayed trans and gauche sequences. Therefore, the 1466 cm^{-1} trans band intensity decreases and the 1457 cm^{-1} gauche band increases with temperature increasing. The similar variation behavior has also been observed in N-octadecylated polybenzamide comblike polymers.[29] Furthermore, the frequency region of CH_2 stretching modes (not shown

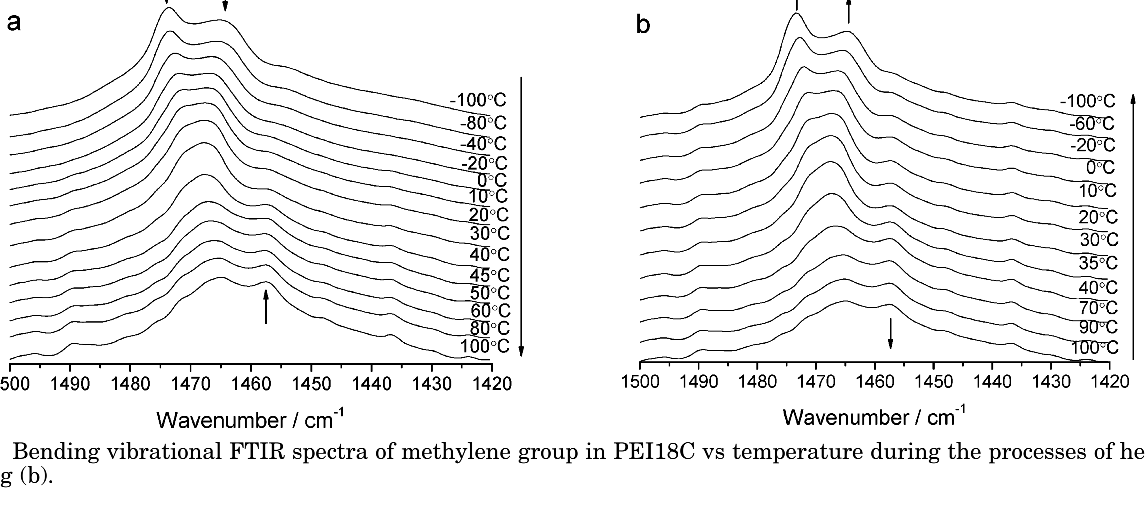


Figure 7. Bending vibrational FTIR spectra of methylene group in PEI18C vs temperature during the processes of heating (a) and cooling (b).

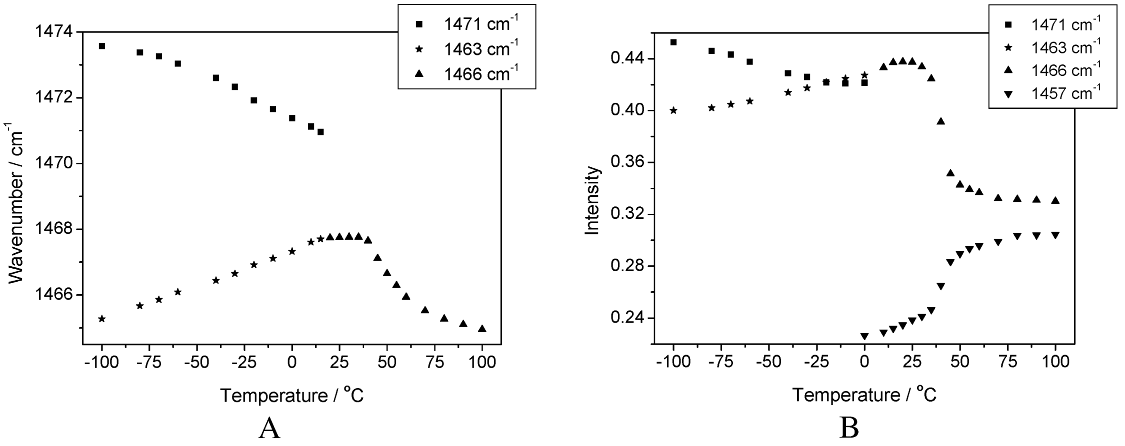


Figure 8. Variation of the peak positions (a) and the absorption intensities (b) of CH_2 bending band in PEI18C with temperature.

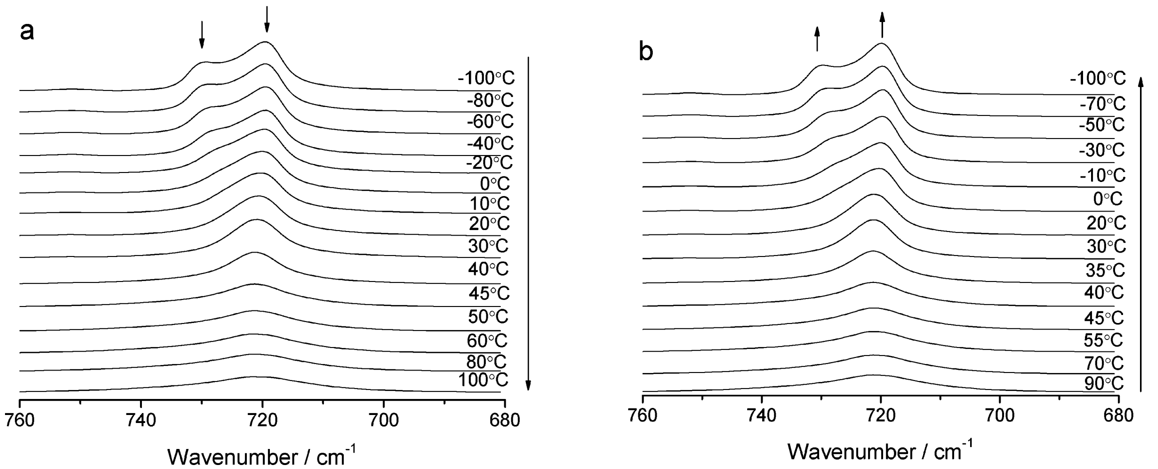


Figure 9. Rocking vibrational bands of methylene group in PEI18C vs temperature during the process of heating (a) and cooling (b).

here) also showed the same variation behavior as that of conformational bands with temperature increasing. For the cooling process (Figure 7b), a reverse behavior was observed in the CH_2 bending vibrational region, meaning that the transition processes of orthorhombic-to-hexagonal and hexagonal-to-melt are reproducible with temperature variation.

To better understand the transition processes of orthorhombic-to-hexagonal and hexagonal-to-melt in PEI18C, both the peak positions and the absorption intensities of the bands 1471, 1466, and 1463 cm^{-1} were plotted as a function of temperatures (Figure 8). As shown in Figure 8a, the 1471 cm^{-1} band, characteristic of orthorhombic crystalline lattice, shifts to lower frequency with temperature increasing and finally disappears at room temperature, while the 1463 cm^{-1} band shifts to higher frequency and finally also vanishes at room temperature. Meanwhile, the hexagonal band at 1466 cm^{-1} appears, and with temperature further increasing, a second new band at 1457 cm^{-1} emerges (not shown in Figure 8a), corresponding to the gauche mode of CH_2 group. The above band variations of methylene groups confirm the phase transition from orthorhombic to hexagonal and from hexagonal to melt state at last. The variation of the absorption intensity of the fours bands, 1471, 1466, 1463, and 1457 cm^{-1}, also reflects the same trends for the phase transition of PEI18C (Figure 8b).

(b) CH_2 Rocking Vibrational Region. In FTIR spectroscopy, the different crystalline modifications of long aliphatic hydrocarbons are characterized by specific absorption bands. A doublet at 720/730 cm^{-1} can be correlated to $\gamma_r(CH_2)$ of orthorhombic packing, while a single band at 720 or 717 cm^{-1}can be correlated with $\gamma_r(CH_2)$ of hexagonal or triclinic packing, respectively, and the band at 723 cm^{-1} is assigned to $\gamma_r(CH_2)$ of the amorphous part.[66,67] As for PEI18C, increasing temperature led to the decrease of the relative intensity of 730 cm^{-1} band (Figure 9a), which is the characteristic of orthorhombic crystal of methylene chains, while the 720 cm^{-1} peak almost keeps at the same position accompanied by the intensity drop because of melting behavior. On the contrary, decreasing temperature enhanced the splitting of the $\gamma_r(CH_2)$ mode into two components at 730 and 720 cm^{-1} (Figure 9b), arising from the interactions between adjacent molecular chains in the crystalline phase, which results in both an in-phase and an out-of-phase rocking mode. Therefore, the splitting of IR rocking vibrational band suggests the symmetrical molecular alignment and the symmetrical direction of molecular vibration in the crystal lattice. It should be noted that the absorption peak at 730 cm^{-1} vanished after the orthorhombic crystal lattice was fully transformed to a hexagonal one,[68] and only a broad absorption peak at 720 cm^{-1} can be observed at high temperature. This result indicates that with temperature increasing, the ordered trans conformation (trans conformation aligned symmetrically in the orthorhombic phase) of PEI18C molecules is changed to the disordered

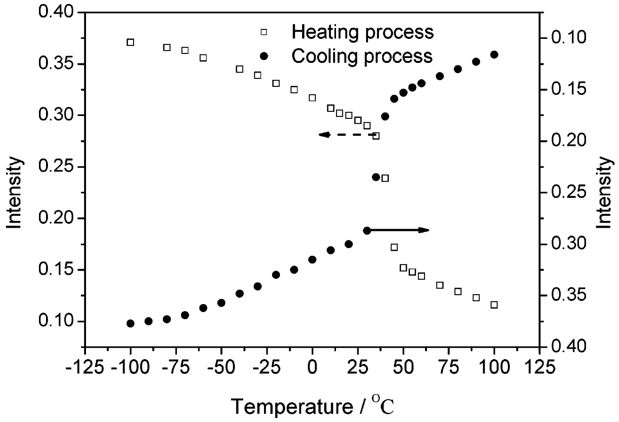


Figure 10. Variation of the absorption intensity of CH_2 rocking band (720 cm^{-1}) in the alkyl side chains of PEI18C with temperature.

trans conformation (trans conformation aligned asymmetrically in the hexagonal phase), so the doublet γ_r-(CH_2) absorption band is changed to a single peak at 720 cm^{-1}.

To clearly express the transition tendency of the crystalline phase of the alkyl side chains in PEI18C comblike polymer, the absorption intensity of 720 cm^{-1} peak was plotted as a function of temperature both in heating and cooling process (Figure 10). As shown in Figure 10, the absorbance at 720 cm^{-1} decreases with temperature increasing, and a temperature transition region between 25 and 60 °C, which corresponds to the hexagonal-melt phase transition, was observed, and vice versa. This result is in good agreement with that of DSC measurement and can also be compared with the variation trend of conformational band (see Figure 7a). From the viewpoint of conformational transformation, at the melting temperature of hexagonal phase, the disordering of the trans conformation is completed, so the peak position of 720 cm^{-1} will not change anymore but the intensity becomes weaker and weaker with temperature rising. However, we cannot fully understand why the orthorhombic−hexagonal transition of the alkyl side chains in PEI(n)Cs could not be obviously detected on DSC plot (see Figure 2). It is provisionally suggested here that the smaller enthalpy of orthorhombic−hexagonal phase transition might contribute to this fact, because even for PEI20C (phase transition enthalpy of PEI18C not detected), only an enthalpy value of 1 kJ/mol was measured for the orthorhombic-to-hexagonal phase transition. Therefore, we can come to the temporary conclusion that DSC methodology is insensitive to such a small enthalpy change, so the orthorhombic−hexagonal phase transition could not be observed.

To establish the relationship between the variation of FTIR absorbance and the DSC thermogram, the combinational results of absorption intensity of 1471, 1463, 1466, 1457, and 720 cm^{-1} peaks and the DSC thermogram of PEI18C with temperature increasing are given in Figure 11. It is observed that the phase transformation temperature falls into a similar temperature region (25−60 °C) for the two characterization methods, confirming that there exist both phase transformation and conformational transition in PEI18C comblike polymer.

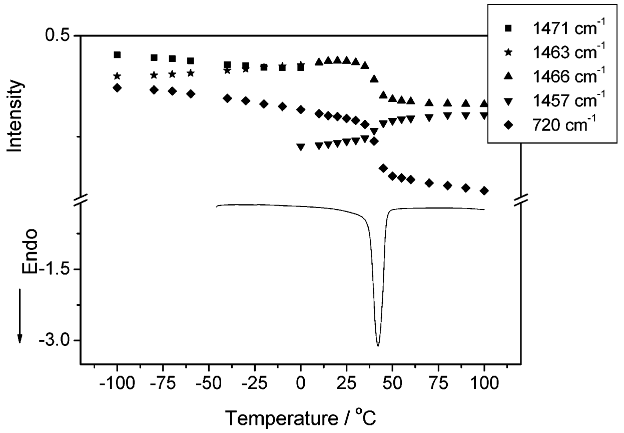


Figure 11. Comparison of the absorption intensity of methylene group in the alkyl side chains with the heat flow of PEI18C during heating process.

Conclusions

Symmetrically substituted PEI derivatives with n-alkyl side groups containing 12 to 20 carbon atoms have been studied in solid state by combination of DSC, WAXD and FTIR spectroscopy. DSC thermograms revealed that the heat enthalpy increases with increasing the length of alkyl side chains, and the melting temperature of the side-chain crystallite increases correspondingly. The orthorhombic-to-hexagonal and hexagonal-to-melt phase transitions were characterized in details by both WAXD and FTIR spectroscopy, and the hexagonal phase was confirmed to exist as an intermediate state in PEI(n)Cs comblike polymers.

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