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Order−disorder transition in eicosylated polyethyleneimine comblike polymers

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Abstract

Order−disorder transition (ODT) behavior in eicosylated polyethyleneimine (PEI20C) comblike polymer obtained by grafting *n*-eicosyl group on polyethyleneimine backbone was systematically investigated by the combination of differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), Fourier transform infrared (FTIR) spectroscopy as well as solid-state high resolution nuclear magnetic resonance (NMR) spectroscopy. DSC investigations showed two obvious transitions, assigned to the transitions (1) from orthorhombic to hexagonal and (2) from hexagonal to amorphous phase, respectively. These transitions are induced by the variations of alkyl side chain conformation and packing structure with temperature changing, which consequently lead to the destruction of original phase equilibrium. The ODT behavior can also be confirmed by spectroscopic methods like WAXD, FTIR and NMR. The ordered structure and the transition behavior of the alkyl side chains confined by the PEI backbone are obviously different from those of pristine normal alkanes. The transition mechanism of ODT and the origin of the phase transition behavior in PEI20C comblike polymer were discussed in detail in this paper.

Keywords: Order−disorder transition; Eicosylated polyethyleneimine; Comblike polymer

1. Introduction

Comblike polymers have been studied extensively in the recent years and continue to attract interests of polymer chemists and material scientists [1−15]. Composed of at least two different structure units of backbone and side chain, these copolymers in solid state are prone to self-assembly into various ordered structures and crystallization behaviors. Therefore, the structure−property correlation, side-chain crystallization behaviors of comblike polymers are of interesting research topics and have been widely studied by various techniques from both pure academic viewpoint and practical applications.

One of the most interesting research topics in comblike polymers is the molecular mobility of polymethylene chain, which can effectively understand the packing mode of alkyl side chains grafted on the backbones [12−15]. In general, the packing mode and the crystallization ability of comblike polymers mainly depend on the polymer backbone structures and the length of the alkyl side chains [1]. Furthermore, the crystallization behavior and conformational ordering of the alkyl 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 [16]. Most obviously, the alkyl side chains, which have profound influence on the microstructure of the comblike polymers, can introduce some unique properties such as solvatochromic

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behavior and reversible thermochromic transition between low and high-temperature solid-state phases [17]. Although considerable progress has been made in explaining the crystal structure and the ordered packing mode of comblike polymers, there are still some key points to be further understood. For example, for conventional comblike polymers, it was suggested that the crystalline structure formed by alkyl side chains is hexagonally packed when the length of the side chain exceeds a critical carbon number (crystallizable carbon atom number) [18–22]. In fact, however, the number of crystallizable carbon atoms on the alkyl side chains is mainly determined by the polymer backbone structure, e.g., flexible polymer backbone can easily induce most part of the alkyl side chains into crystallization by adjusting their backbone conformational state [23,24].

With the extensive study interests in comblike polymers nowadays, it becomes a reconsidered question whether the comblike polymer consisting of a long hydrophobic side chain has only hexagonal crystal modification or not. In fact, the answer is no. It has been shown that except hexagonal crystal, orthorhombic and triclinic crystallization modifications can also be observed from a same comblike polymer. Benedetti et al. studied the spectral changes of poly(octadecyl ethylene oxide) and isotactic poly(octadecyl ethylene) by FTIR technique, and found that when experimental temperature is sufficiently low, the orthorhombic to hexagonal transition can be observed in a wide temperature range [25]. It is a pity that, however, they did not give detailed explanation about the phase transition of the alkyl side chain from the viewpoint of the molecular mobility. Jones studied the crystal structure changes of isotactic polyolefins by X-ray method [26], and the experimental results showed that the different crystal modifications can be observed for the comblike polymer containing specific number of carbon atoms (n). For $n > 14$, orthorhombic packing mode can be found, while for $n < 14$ hexagonal crystal structure dominates. These authors also found that the alkyl side chains take different conformational states in the two crystal modifications. Lee et al. synthesized a series of cellulose derivatives by reacting hydroxypropylcellulose (HPC) with alkyl isocyanates and analyzed the side-chain crystallization behavior of these alkyl-substituted semiflexible polymers by WAXD [27,28]. The alkyl groups in C12HPC crystallize in a form similar to triclinic crystal of paraffins, but multiple crystalline modifications coexist in C18HPC. As for the systems of polyelectrolyte–surfactant self-assembly supramolecules, Brinke [13–15,29–31] and Antonietti et al. [32–35] investigated the self-organized structure of the comb-shaped supramolecule architecture based on the combination of hydrogen bonding and electrostatic interactions. Multiple phase behaviors were observed, including the formation of cubic, hexagonally ordered cylinders and lamellar morphologies when the blend ratio between the host and the guest was adjusted. Although lots of phase behaviors have been observed in self-assembly supramolecules via hydrogen bonding, ionic bonding and coordination bonding, the phase behavior of comblike polymers formed by covalent bonding has been seldom reported.

In the previous work, we have systemically studied the conformational variation and phase transition behavior of PBA(n)C [23] and PEI(n)C [24] comblike polymers. Experimental results showed that the crystal structure and phase behavior of the alkyl side chains in these two kinds of comblike polymers are quite different, which are attributed to the rigidity difference of the main chain backbones. In the present research, we focused on *N*-eicosylated polyethyleneimine (PEI20C) comblike polymer with flexible backbone, and investigated the order–disorder transition of the alkyl side chains grafted on the backbones by the combination of differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), Fourier transform infrared (FTIR) spectroscopy and solid-state high resolution nuclear magnetic resonance (NMR) spectroscopy. More specifically, it is also of fundamental importance to elucidate the origin of the peculiar phase transition behavior of this sort of comblike polymer and to establish an integration spectroscopic method for characterizing the crystalline structure of comblike polymers.

2. Experimental section

2.1. Preparation of N-eicosylated PEI

The preparation method of *N*-alkylated PEI comblike polymers has been described in detail elsewhere [24], and will not be explained in this paper. In brief, the *N*-eicosylated PEI (PEI20C) sample was synthesized by a homogeneous reaction of polyethyleneimine (PEI) with *n*-eicosyl bromide in hot tetrahydrofuran (THF). By this method, a reasonable yield of alkylated PEI can be achieved. The alkylation degree was determined to be 47% by elemental analysis.

2.2. Characterization

2.2.1. Differential scanning calorimetry (DSC)

DSC 2910 (TA Instruments), calibrated with indium, was used to study the thermal behavior of PEI20C. Specimens of 3–5 mg were encapsulated in aluminum pans and heated from −50 to 100 °C, and kept at 100 °C for 5 min, subsequently cooled down to −50 °C and kept at −50 °C for 5 min, and then heated again from −50 to 100 °C. The heating or cooling rate was 10 °C/min in all thermal processes. The second heating DSC thermograms were recorded.

2.2.2. Wide-angle X-ray diffraction (WAXD)

WAXD measurements were performed on a Rigaku D/max-2500 X-ray diffractometer over a temperature range of −90 to 100 °C, using Cu Kα radiation (1.542 Å), power of 200 mA/40 kV, and rotating angle $2\theta = 1°–40°$.

2.2.3. Variable temperature Fourier transform infrared (VT-FTIR) spectroscopy

PEI20C was grinding-mixed with KBr powders and then pressed into thin pellet. IR spectra were measured on a Bruker Equinox 55 spectrometer equipped with a temperature-variable cell and the obtained spectra were processed by a

Bruker OPUS program. The temperature-variable cell was kept in vacuum and liquid nitrogen was used as coolant. A resolution of 2 cm^{-1} was chosen and 64 scans were accumulated. IR spectra were recorded in the temperature range of −70 to 100 °C during the heating and cooling processes. At every temperature point for IR spectral collection, the samples were equilibrated for 5–8 min before spectral collection.

2.2.4. Temperature dependent solid-state nuclear magnetic resonance (NMR) spectroscopy

Solid-state high resolution ^{13}C CP/MAS (cross polarization/magic angle spinning) NMR spectroscopic investigation was performed on a Bruker AM300 spectrometer at 75.4 MHz, operated at magnetic field of 7.05 T and spinning speed of 4 kHz. 5 μs 90° pulse was used for ^{13}C NMR spectra, and the contact time for the cross polarization process was 1 ms at a recycle delay time of 2 s. The NMR spectra were recorded in the temperature range of 25–70 °C. The chemical shift of adamantine (38.5 ppm) was used as the standard to calibrate the chemical shift values of PEI20C comblike polymer.

3. Results and discussion

3.1. Thermal behavior of PEI20C comblike polymer

In our previous investigations [24], the order–disorder transition (ODT) from well-ordered orthorhombic phase to less-ordered hexagonal phase cannot be observed for PEI(n)C (for $n = 12$–18) comblike polymers. In the present work, however, ODT can be detected for PEI20C by several methods, among which DSC is a simple and effective tool to characterize the phase changes of alkyl side chains.

DSC results showed that there are three endothermic peaks for PEI20C during the heating process (Fig. 1). The first endothermal peak, centered at 15.8 °C (marked by dashed circle in Fig. 1), which is obviously different from that of PEI18C [24], is assigned to the phase transition from orthorhombic to hexagonal phase. Another two endothermal peaks, observed at 41.2 and 51.9 °C during the heating process, are assigned to the transitions from hexagonal to molten state. According to Zerbi et al. [36], both the phase transition enthalpy (from orthorhombic to hexagonal phase) and melt enthalpy (from hexagonal to molten state) are much lower than that of pure n-nonadecane, indicating that alkyl side chain confined on the PEI backbone formed the lower ordered packing structure and imperfect crystal. The detailed investigation on this packing structure and crystalline state was given by WAXD, FTIR and solid-state NMR spectroscopy.

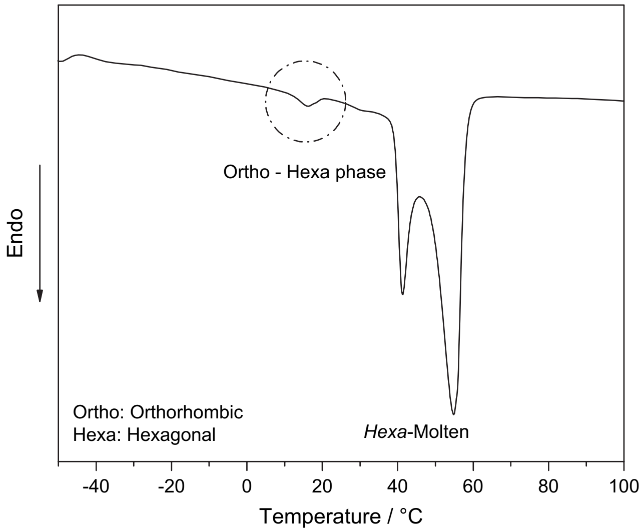

Fig. 1. DSC heating thermograms of PEI20C at a heating rate of 10 °C/min.

3.2. Wide-angle X-ray diffraction of PEI20C

According to DSC data, PEI20C comblike polymer exhibits orthorhombic and hexagonal crystal transition at different temperature regions. To detect the packing structure of alkyl side chain, temperature-variable WAXD measurement was performed from −90 to 100 °C (Fig. 2). As shown in Fig. 2, orthorhombic and hexagonal characteristic peaks, centered at $2\theta = 23.4°$ ($d = 3.8$ Å) and $2\theta = 21.4°$ ($d = 4.2$ Å), can be observed in the range of −90 to 20 °C [37]. With temperature increasing from −90 to 20 °C, the intensity of orthorhombic phase (23.4° diffraction peak) gradually decreased and finally disappeared, which is well consistent with the DSC result that the endothermal process occurred at 15.8 °C is induced by the vanishing of ordered orthorhombic crystal. For hexagonal phase (21.4° diffraction peak), the intensity nearly keeps constant with the orthorhombic phase decreasing. When the temperature further increased, the intensity of hexagonal phase began to decrease and finally changed into a broad peak at smaller angle ($2\theta = 19.3°$, $d = 4.6$ Å), indicating that the alkyl side chains were entirely transformed to amorphous state. The measured temperature transition region from hexagonal phase to molten state by WAXD is in good agreement with that of DSC result (41.2/51.9 °C). Therefore, WAXD result confirms without doubt that the observed endothermal transition

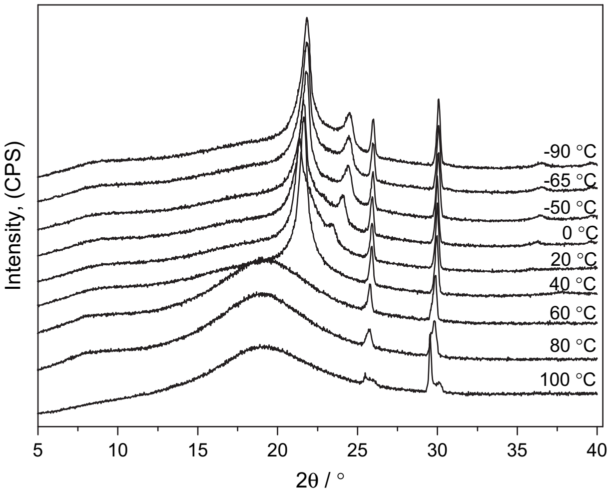

Fig. 2. Temperature-variable WAXD results of PEI20C.

(41.2/51.9 °C) in DSC thermograms was attributed to the transition from hexagonal phase to molten state. It should be noted that, however, the layered structure ($2\theta = 26°$ and 30°) formed by alkyl side chains in PEI20C did not disappear with the melting of the crystal structure [24], indicating that the framework composed of PEI backbone did not collapse with crystalline structure disappearing. In addition, the WAXD result of poly(β-L-aspartate) containing linear alkyl side chains also gave the strong supports to our result, for which the disappearance of the sharp diffraction peak in the wide-angle region was clearly assigned to the fusion of the paraffinic crystallites [5].

3.3. Variable temperature FTIR (VT-FTIR) spectroscopy

As observed from DSC and WAXD experiments, obvious thermal transition and crystalline structure transition can be detected for PEI20C comblike polymer; however, the conformational variation behavior and the packing mode of the alkyl side chains in this polymer cannot be characterized by the above two techniques. Therefore, in order to in-depth interpret the phase transition and macromolecular chain mobility in comblike polymers, FTIR experiments were carried out. Fig. 3 shows the VT-FTIR spectra of PEI20C in the range of 1500–1420 cm^{-1}.

As shown in Fig. 3, with temperature increasing from −70 to 30 °C, the intensity of the ordered *trans* conformational bands (1471 and 1463 cm^{-1}), characteristic of orthorhombic structure [38–40], decreased; as temperature exceeded 30 °C, these two bands fully disappeared, and a new band at 1466 cm^{-1}, characteristic of hexagonal structure, emerged in the temperature range of 30–100 °C. CH_2 *gauche* conformational band (1457 cm^{-1}), characteristic of amorphous state, was detected when temperature was higher than 30 °C. As shown in Fig. 3, the intensity of the disordered *trans* conformation band at 1466 cm^{-1} gradually decreased with temperature increasing, while that of the *gauche* conformational band at 1457 cm^{-1} increased. From DSC and WAXD result, orthorhombic phase is firstly transformed to hexagonal phase and then to the molten state with temperature increasing during the phase transition process of PEI20C. Correspondingly, FTIR also confirmed that the conformational ordered packing structure of the CH_2 group (1471/1463 cm^{-1}) was transformed to the conformational disordered structure (1466 cm^{-1}), and finally to the amorphous state (1457 cm^{-1}). These conformational variations are similar to the orthorhombic–hexagonal–molten state transition behaviors of $C_{29}H_{60}$ [41,42], constrained PE [43,44]. The investigation on the conformational variation behavior of these comblike polymers further showed that the flexible polymer backbone can improve the crystallinity of alkyl side chains and generate more ordered crystalline structure. Similarly, the reverse change phenomenon of CH_2 conformational bands can also be observed in the cooling process (not shown here), meaning that the mobility, conformational mode and phase behavior of the alkyl side chains grafted on the PEI backbone are adjustable with temperature increasing or decreasing.

Fig. 4 shows the IR spectra of CH_2 rocking band of PEI20C in the region of 750–690 cm^{-1} as a function of temperature. According to previous report on high density polyethylene (HDPE) [45], we know that a doublet at 719/730 cm^{-1} is correlated to $\gamma_r(CH_2)$ of orthorhombic packing form, while a single band at 720 or 717 cm^{-1} is assigned to $\gamma_r(CH_2)$ of hexagonal or triclinic packing form, respectively, and the band at 723 cm^{-1} to $\gamma_r(CH_2)$ of the amorphous part. In Fig. 4, a doublet peak at 719/730 cm^{-1} appears at low temperature, characteristic of the orthorhombic packing mode of eicosyl side chain on the PEI backbone. Compared with that of PEI18C [24], the absorption intensity and the band variation trend of PEI20C with temperature are more easily observed, indicating that the crystalline structure formed by longer alkyl side chains is much more ordered than that of shorter ones. As temperature increases, the two bands of 719 and 730 cm^{-1}

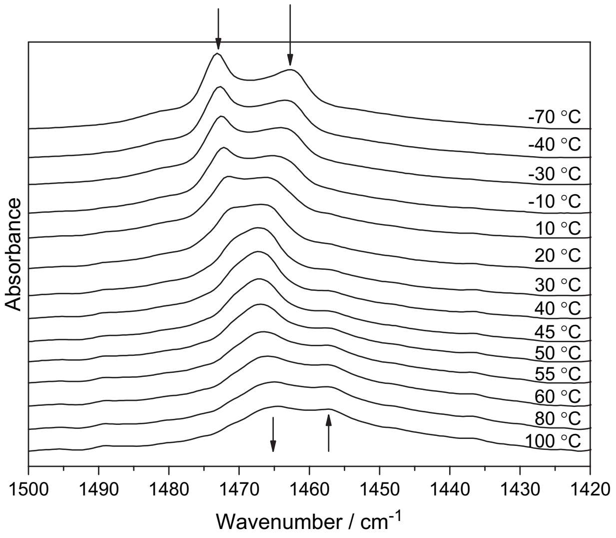

Fig. 3. Bending vibrational VT-FTIR spectra of CH_2 in PEI20C in the heating process.

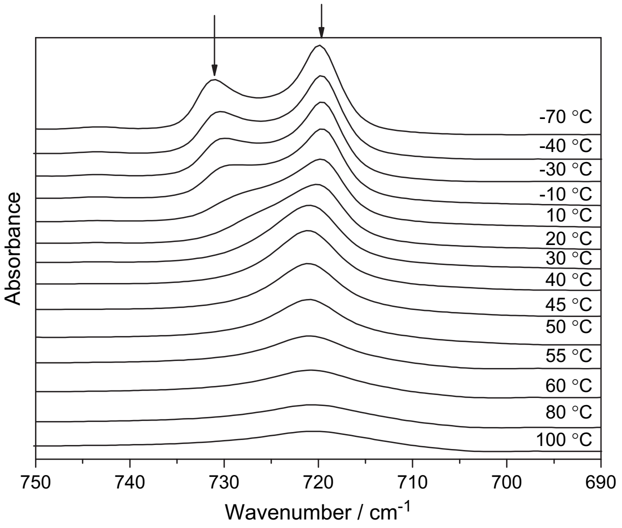

Fig. 4. Variation of the rocking vibrational band of CH_2 in PEI20C versus temperature in the heating process.

gradually became wider and weaker, exhibiting a blue shift and red shift, respectively. This variation phenomenon of CH_2 rocking bands in PEI20C is different from that of HDPE [46] and *n*-alkanes [36]. As temperature rose up to 30 °C, 730 cm^{-1} band disappeared and only 720 cm^{-1} band was left, implying that the orthorhombic crystalline structure has been destroyed, or in other words the perfection degree of the crystalline region formed by the alkyl side chains was decreased. With temperature further increasing ($T > 30$ °C), hexagonal mesophase was gradually transformed into the amorphous state ($T > 60$ °C). Therefore, VT-FTIR spectroscopy also gave the same conclusion as that of DSC and WAXD, i.e., the crystallization structure in PEI20C does not directly transform from the ordered structure to the amorphous state, but firstly to the metastable structure (hexagonal mesophase) and then to the liquid state.

In order to further understand the order–disorder transition behavior of the alkyl side chains in PEI20C comblike polymer, the absorption intensities of the $\delta(CH_2)$ and the $\gamma_r(CH_2)$ bands are correlated with the DSC thermogram of PEI20C (Fig. 5). The two obvious transitions are marked by regions I and II. In the two transition regions, DSC and FTIR data are in very good agreement, suggesting that the melting process of PEI20C comblike polymer is not directly transformed from an ordered structure to amorphous state, but firstly enters conformational metastable state and then to the coexisting state of irregular *trans* and *gauche* conformations.

3.4. Solid-state high resolution NMR spectroscopy

Solid-state NMR spectroscopy is a very powerful technique to elucidate phase structures and macromolecular chain motions of polymeric materials, and used here to understand the conformational transition of alkyl side chains in PEI20C. It is well known that the ^{13}C NMR chemical shift of int-CH_2 in polyethylene and paraffins is a good expression for the crystal structure variation. It has already been reported that the ^{13}C NMR chemical shift values of 30, 33 and 34 ppm correspond to the coexisting state of *trans* and *gauche* conformations in amorphous, orthorhombic and triclinic forms, respectively [47–51]. The expended ^{13}C CP/MAS NMR spectra of the side chain carbons of PEI20C as a function of temperature are shown in Fig. 6, and the peak assignments are labeled in the figure. Due to the experimental time limitation, the temperature dependent solid-state NMR spectral measurement was only performed in the temperature range of 25–70 °C. As $T = 25$ and 35 °C, the peak corresponding to the inner methylenes in the *trans* conformation appears at 33 ppm, whereas at $T = 70$ °C, the peak is upfield displaced to 30 ppm as is expected for a polymethylene chain undergoing a fast transition between the *trans* and *gauche* conformers. At intermediate temperatures, the *trans* and *gauche* conformations are in a changing state, and its intensity changes show the reversible behavior. In addition, the obvious change taking place at around 45 °C indicated that after the orthorhombic crystal structure disappeared, the ordered conformation state entered the coexisting state of ordered and disordered structures. Furthermore, the methyl peak at 15 ppm vanished with temperature increasing, which might be induced by the enhanced mobility of the alkyl side chains, resulting in the entire side chain entering into the molten state. The transition behavior of PEI20C described by NMR is similar to that of comblike poly(α-alkyl β,L-aspartate)s [5,52,53] and poly(α-alkyl γ-glutamate)s [8,9,54]. The obtained temperature transition region from ^{13}C CP/MAS NMR spectra is in good agreement with that of DSC, WAXD, and FTIR, thus further confirming the existence of the ODT in PEI20C comblike polymer.

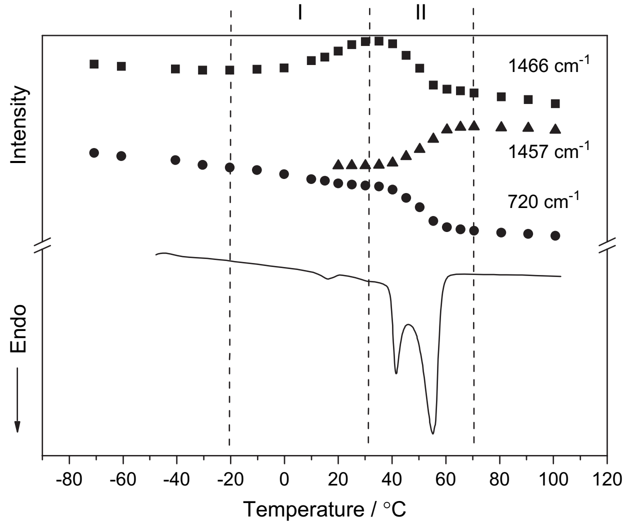

Fig. 5. Comparison of the absorption intensity of CH_2 group in the alkyl side chains with the heat flow of PEI20C in the heating process.

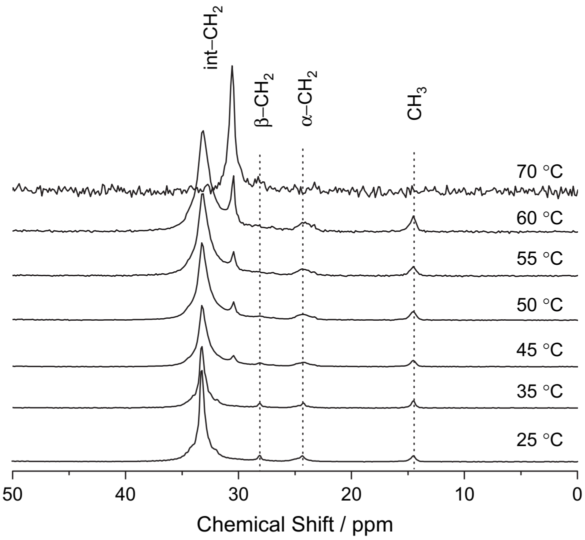

Fig. 6. ^{13}C CP/MAS solid-state NMR spectra of PEI20C as a function of temperature.

4. Conclusions

In this paper we have systematically studied the order–disorder transition behaviors of PEI20C by using the methods of DSC, WAXD, FTIR, solid-state high resolution NMR spectroscopy to investigate the phase behavior and conformational transition of the alkyl side chains, aiming to explain the mechanism of the order–disorder transition.

The order–disorder transition of PEI20C has been detected by DSC method, and two crystalline phases were proved to exist: one is a well-ordered phase (orthorhombic lattice) and the other is a less-ordered phase (hexagonal metastable structure). Compared with the phase transition behavior of PEI18C [24], it is indicative of the major modification of the crystal structure with an increase in the length of the alkyl side chain. This conclusion is also supported by WAXD, FTIR and solid-state NMR experiments. All the experimental results strongly suggest that the melting process of PEI20C sample is not directly transformed from an ordered structure to amorphous state, but firstly enters conformational metastable state and then to the coexisting state of irregular *trans* and *gauche* conformations.

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