Effect of Main-Chain Rigidity on the Phase Transitional Behavior of Comblike Polymers

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ABSTRACT: The influence of the rigidity of polymer backbones on the side-chain crystallization and phase transition behavior was systematically investigated by a combination of differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), Fourier transform infrared spectroscopy (FTIR), and high-resolution solid-state nuclear magnetic resonance spectroscopy (NMR). DSC investigation indicated that the crystallization number of alkyl carbon atoms of the side chains grafted onto the rigid polymer backbone, poly(*p*-benzamide) (PBA), is much lower than that of the alkyl carbon atoms of the side chains grafted onto the flexible polymer backbone, poly(ethyleneimine) (PEI), implying that the conformational state of the polymer backbones has a strong effect on the side-chain crystallization behavior in comblike polymers. WAXD and FTIR results proved that these two comblike polymers pack into hexagonal (PBA18C) and orthorhombic (PEI18C) crystals, respectively, depending on the adjusting ability of the polymer backbones for particular conformational states. It was also found that the presence of the crystalline−amorphous interphase ($\delta = 31.6$ ppm) in PBA18C detected by solid-state ^{13}C NMR spectroscopy can be attributed to the rigid PBA backbone, which restricts the mobility of the alkyl side chains. The conformation effect of the polymer backbones and the packing mode variation of alkyl side chains are explicitly discussed in terms of molecular chain mobility and theory of macromolecular chain conformation.

Introduction

Comblike polymers have been studied extensively within the recent years and are still attracting a lot of research interests.[1−17] Composed of at least two different units, the backbone and the side chain, these copolymers are prone to self-assembly into various ordered structures and show characteristic crystallization behaviors in the solid state. Therefore, the crystallization behavior and conformational variations of the alkyl side chains in comblike polymers are interesting topics and have been widely studied from both academic viewpoint and practical applications.

Confined by polymer backbones with characteristic rigidity, alkyl side chains may undergo quite different conformational transitions and crystallization processes. This provides a possible way to the preparation of comblike polymer materials with specific performances. The packing modes and the crystallization behavior of comblike polymers are generally considered to be determined by the length of the *n*-alkyl side chains.[1,4,6−10] The alkyl side chains have another profound influence on comblike polymers, e.g., they can act as “solvent” of the polymer backbones, which induces solvate chromic behavior and reversible thermochromic transition of solid-state phases between low and high temperatures.[18] Jordan compared the thermal transition behavior of the flexible comblike polymers, such as poly(*n*-alkyl acrylate)s and poly(*n*-alkyl acrylamide)s,[2,3] and found that the thermal enthalpies of poly(*n*-alkyl acrylamide)s are lower than that of poly(*n*-alkyl acrylate)s. This was ascribed to the smaller numbers of CH_2 units incorporated into the crystal lattice. Platé and Shibaev analyzed the crystal structures and packing modes of poly(*n*-alkyl acrylate)s and concluded that alkyl side chains grafted onto the flexible polymer backbones pack into hexagonal crystals.[4] Similarly, by comparing the side-group crystallization ability of poly(*n*-alkyl acrylate)s and poly(*n*-alkyl methacrylate)s,[5] Morawetz found that the crystal structures of the two comblike polymers are mainly determined by the conformational state of the backbones. Recently, the influence of the polymer backbone conformations on the crystallization behavior of alkyl side chains has drawn scientists’ attention. The cumulative substitution by multiple phenyl and methyl groups on a periodic copolymer backbone as reported by Yokota was found to make the polymer main chain less flexible and unfavorable for the side-chain crystallization.[19] In other words, the side chains can crystallize easier at a flexible backbone than at a rigid one. The author did not pay attention to the phase transition behavior of the alkyl side chains. Inomata compared the crystallization behavior of methacrylic and acrylic graft copolymers (PMMA-*graft*-PEG and PMAc-*graft*-PEG) with PEG side chains[20] and concluded that, as a consequence of the side-chain crystallization, the rearrangement of the main-chain conformation is limited for rigid main chains, while the flexible main chains could change their conformation much easier. Similarly, Shibasaki studied the side-chain crystallization of the fluorinated *n*-alkyl acrylate and methacrylate comblike polymers[21] and found that the side groups grafted onto the flexible main chain can easily crystallize into a crystal lattice.

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Although some investigations on the effect of the main-chain structure on the crystallization behavior of side alkyl chains have been published, only very little information is available on the influence of the main-chain rigidity on the conformational variation and phase behavior of alkyl side chains, especially from the viewpoint of infrared spectroscopic characteristics and molecular chain mobility. We previously studied the conformational variation and phase transition behavior of PBA(*n*)C and PEI(*n*)C comblike polymers.[22,23] The crystalline structure and phase behavior of the alkyl side chains in these two comblike polymers are differentiated. In the present study, we focus on the comparison investigation of the effect of main-chain rigidity on the conformational state and phase transitions of comblike copolymers with a rigid backbone (N-octadecylated poly(*p*-benzamide, PBA18C) and with a flexible backbone (N-octadecylated poly(ethyleneimine), PEI18C) with the same alkyl side chain (C18). The two copolymers were investigated by the combination of differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), Fourier transform infrared (FTIR) spectroscopy, and high-resolution solid-state nuclear magnetic resonance spectroscopy (NMR). The influence of main chain on the alkyl side chains is discussed with respect to the chain packing and the mobility of the molecular chains.

Experimental Section

1. Sample Preparation. The preparation of N-alkylated poly(*p*-benzamide) (PBA) and poly(ethyleneimine) (PEI) comblike polymers has been described elsewhere[22,23] and will not be described in detail here. In brief, the N-octadecylated PBA (PBA18C) and PEI (PEI18C) were synthesized via homogeneous reaction. By this method, a reasonable yield of alkylated PBA and PEI can be achieved. The alkylation degrees of PBA and PEI are 96.9% and 47.0%, respectively.

2. Characterization. Differential Scanning Calorimetry (DSC). A Mettler differential scanning calorimeter (model DSC822), calibrated with indium, was used to study the thermal behavior of the PEI18C and PBA18C samples. Specimens of 3−5 mg were encapsulated in aluminum pans and first heated from −60 to 100 °C and kept at 100 °C for 10 min and then cooled down to −60 °C and kept at −60 °C for another 10 min; finally, the samples were heated again from −60 to 100 °C. The thermograms for the first cooling and second heating runs were recorded. Both the cooling and heating rates are all 10 °C/min.

Variable Temperature Wide-Angle X-ray Diffraction (VT-WAXD). WAXD measurements were performed on a Rigaku D/max-2500 X-ray diffractometer over the temperature range of −90 to 100 °C, using the Cu Kα radiation of 1.542 Å.

Variable Temperature FTIR Spectroscopy (VT-FTIR). The PEI18C and PBA18C were separately dissolved in $CHCl_3$, and the solution was then cast on KBr pellets followed by slow evaporation of the solvent. The FTIR measurements were performed on a Bruker EQUINOX 55 spectrometer equipped with a temperature-variable cell, and the obtained spectra were processed by the 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. Infrared spectra were recorded at temperatures ranging between −100 and 100 °C during heating or cooling process. At every temperature point, the samples were equilibrated for ca. 5−8 min before measurements.

Temperature-Dependent Solid-State Nuclear Magnetic Resonance Spectroscopy (NMR). ^1H and ^{13}C DD/MAS (dipolar-decoupling magic angle spinning) NMR and ^{13}C CP/MAS (cross-polarization magic angle spinning) NMR spectra were recorded at a Bruker DSX 300 spectrometer operating at a magnetic field of 7.05 T. A variable temperature double-resonance 4 mm MAS probe was used. Samples were packed in zirconium dioxide rotors and spun at 4 kHz at variable temperatures. The 90° pulse length was 5 μs for all NMR experiments like ^{13}C NMR, and the contact time for the cross-polarization process was 1 ms. The recycle delay time was 2 s for the ^1H and ^{13}C CP/MAS measurements, but 20 s in the ^{13}C DD/MAS experiments. Spectra were recorded in the temperature range from 25 to 100 °C. Before the NMR experiments, the chemical shift was calibrated to the resonance frequencies of water (^1H NMR) and of adamantane (^{13}C NMR).

Scheme 1. Chemistry Structure of PBA18C (a) and PEI18C (b)

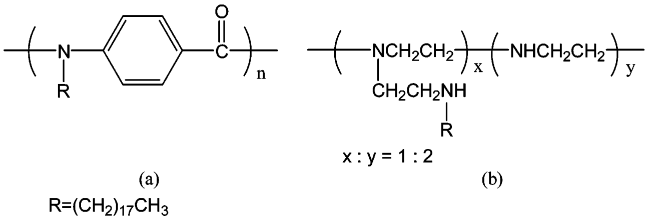

Table 1. Thermodynamic Parameters Calculated from DSC Data for PEI18C and PBA18C

polymer	T_m[a] (K)	ΔH_m (kJ/mol)	ΔS_m[b] (kJ/(mol K))	N_c[c]
PEI18C	311.6	28.93	0.0928	11.57
PBA18C	284.6	17.45	0.0613	5.68

[a] Peak melting temperature. [b] Entropy changes estimated by $\Delta S_m = \Delta H_m/T_m$. [c] Number of crystallized methylene groups, calculated by using $\Delta H =$ 3.07 kJ/mol per CH_2 unit, estimated for normal alkanes.[28]

Results and Discussion

Chemical Structure of PBA18C and PEI18C. The analysis of chemical structure can provide some good references and supporting information for experimental results. Because PBA18C and PEI18C have different molecular structures, their structural analysis will be more important in the aspects of comparing the effect of their backbones on the phase transition and crystallization behaviors of side alkyl chains grafted onto PBA and PEI backbones (Scheme 1). It is well-known that PBA molecules belong to the family of aromatic polyamides, while PEI belongs to the aliphatic polyamides, implying that their structural differences will greatly affect the crystallization behavior of side alkyl chains. Comparing the chemical structure of side alkyl chains attachment via N sites onto polymer backbones, it is clear that the alkyl side chains substituted on PBA molecules should have harder mobility and lower crystallinity due to side chains directly linked with rigid polymer backbone, while those attached on PEI were more flexible and easily adjusted their conformational states. Although side alkyl chains were both substituted on N sites, the different effect of polymer main chains on side alkyl chains will be observed in the aspects of thermal behavior, crystal structure, phase transition, and conformational variations because of the different energy barriers to rotation existing in CH_2 segments.

Simply speaking, for these two types of substitution the spacing between side alkyl chains along polymer backbone is different according to their heavy atoms between two neighboring octadecyl side chains. For PBA18C, it is easily calculated that PBA monomer has nine heavy atoms in one structural unit (Scheme 1), so each octadecyl chain has to packing in a way that also combines nine external heavy atoms to be nearby. In the present study, however, branched PEI molecules were selected as the host of side alkyl chains. According to PEI structural chemistry, the ratio of N, NH, and NH_2 was 1:2:1, and the alkylation progress was observed in N sites of NH_2 along PEI main chain. In view of the specific structural feature of PEI molecules, the spacing of C18 along PEI molecules possibly has 9 or 12 heavy atoms due to their different connection ways. Comparing the difference between the heavy carbon atoms per C18 along the PBA and PEI main chains, it is clear that although

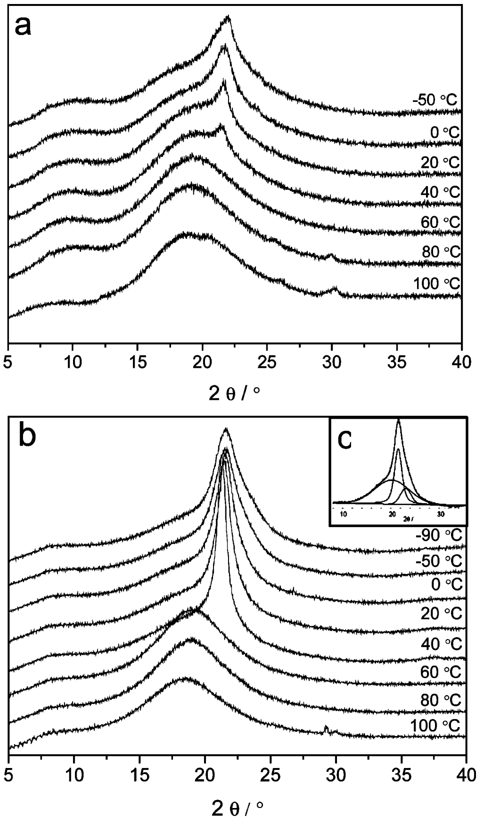

Figure 1. Temperature variable WAXD results of comblike polymers in the heating process: (a) PBA18C, (b) PEI18C, (c) curve-fitting result of PEI18C at −90 °C.

the occurrence of the larger number of noncrystallizing heavy atoms between octadecy side chains, the crystal stability will be improved in PEI than that of PBA, implying that longer spacing between side alkyl chains or more flexible polymer main chains will easily improve the mobility of side chains and enhance their crystal structural stability. In fact, the distribution of side groups along polymer backbones will probably have influence on the crystallization behavior and crystal structure of side chains confined between main chains. Therefore, because of the complexity of the branching structure of PEI molecules, it is impossible to give the detailed chemistry structure resting on the current characterization methods, but we can postulate that all of the distribution of chemistry structure of both PEI and PEI18C will proceed such a way that improves the crystallinity of side alkyl chains and accommodates much more CH_2 groups in the crystal lattice. So, in the following paragraphs we will gradually confirm our postulation on PBA18C and PEI18C via experimental methods.

Crystallization Behavior of PBA18C and PEI18C. To get more accurate information about the crystallization characters of the alkyl side chains, temperature variation wide-angle X-ray diffraction (WAXD) measurement was carried out (Figure 1). As shown in Figure 1, the diffraction peak centered at 21.4°, which is characteristic for the crystallization of octadecyl side groups, can be found for both samples, PBA18C and PEI18C, under cryogenic conditions. Comparing the diffraction curves of PBA18C (Figure 1a) with those of PEI18C (Figure 1b) in the temperature range of −50 to 40 °C, it is noticed that PBA18C exhibits a much lower ordered crystal structure, revealing that the rigid main chains hinder the regular packing mobility of the side groups, thus leading to a decrease of the side-chain crystallization ability. As temperature decreased to −50 °C, the amorphous phase (20° diffraction peak) can still be detected in PBA18C, further confirming that fewer CH_2 groups enter into the crystalline region. On the contrary, PEI18C exhibits a sharp crystalline peak and smaller half-bandwidth, indicating that the alkyl side groups attached on flexible backbone can easily form ordered structure.

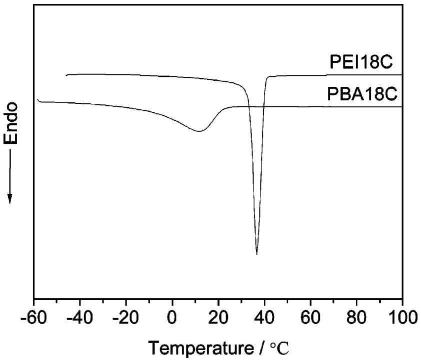

Figure 2. DSC thermograms of PBA18C and PEI18C in the heating process.

According to the previous report, hexagonal, orthorhombic, and triclinic crystal structure can be formed in comblike polymers, and these packing structures depend on the side-chain length and crystallization conditions.[24] In the present study, we found that the conformational state of polymer backbone also plays an important role in the process of alkyl side-chain packing, except crystalline region size and crystal perfection degree. According to the chemistry structural analysis between PBA18C and PEI18C, it is clearly shown in Figure 1 that only partially ordered hexagonal crystal can be seen in PBA18C, while PEI18C exhibits polymorphic structures which showed that rigid polymer main chain will give higher rotation barrier to side alkyl chains. The curve-fitting result at −90 °C showed that amorphous (20°), orthorhombic (23.6°), and hexagonal (21.4°) phases coexist in PEI18C (Figure 1c). As the temperature exceeds the melting temperature of the octadecyl side chains (ca. 40 °C), the intensity of crystal peaks decrease abruptly, and once the temperature is higher than the melting point of the octadecyl side chains in both comblike polymers, the ordered structure vanishes. This result is similar to that one of poly(β-L-aspartate) containing linear alkyl side chains.[25] Here the absence of the sharp diffraction peak in wide-angle region corresponds to the fusion of paraffinic crystallites.

Thermal Behavior of PBA18C and PEI18C. From WAXD results, it is clear that these two polymer derivatives have different crystal structures and crystallinity, implying that the side alkyl chains in PBA and PEI backbones should have different thermal transitional behavior. Figure 2 shows the DSC curves of PBA18C and PEI18C. An obvious endothermic transition in the heating process can be observed, which is ascribed to the melting of the side-chain crystals.[3−5,15−18] Compared with typical crystalline polymers and *n*-alkanes, the melting peaks of these two comblike polymers are obviously different with respect not only to the peak shapes but also for the temperature transition range.[1] For PBA18C, the melting peak of octadecyl side groups is weak and broad and appears at a relatively low-temperature region (11.6 °C in the second heating run); for PEI18C, however, the melting peak is sharp and appears at a relatively high-temperature (38.6 °C in the second heating run). The two different melting temperatures of the octadecyl side groups within these two comblike polymers can be attributed to the different crystal structures and the packing modes of the alkyl side chains. Therefore, a temporary conclusion can be drawn that as the length of alkyl side chain is same, the main-chain structure plays an important role and determines the side-chain crystallization behavior.

The rigidity or flexibility of polymer chains is usually characterized by the persistence length *q* or the exponent in the Mark−Houwink relation. Here, the exponent of the Mark−Houwink relation was used to explain the different thermal behavior of the comblike copolymers PBA18C and PEI18C. For aromatic PBA molecules, the exponent of the Mark−Houwink relation is 1.5 at a molecular weight in the range of 4000−16 000;[26] the exponent of PEI, however, is only 0.31.[27] It is common knowledge that big exponent corresponds to rigid polymer backbones. Therefore, by comparison, we can find that the PBA backbone is more rigid than that of PEI. Consequently, the ability of the PBA backbones for a conformation adjustment to allow the motion or crystallization of the alkyl side chains is much lower than that of PEI. So, the ability of the PBA and PEI backbone conformational adjustment determines the crystal structures of the alkyl side chains. The more rigid PBA backbones restrict the ordered packing of octadecyl side chains into a crystal lattice. This results in a broadening and low-temperature position of the melting peak of octadecyl side chains in the PBA18C comblike polymer.

In order to characterize the effect of the polymer backbone on the side-chain crystallization more quantitatively, Table 1 shows the thermodynamic parameters of PBA18C and PEI18C, which were calculated from DSC data. As shown in Table 1, the calorimetric data of the CH_2 groups at the flexible PEI backbone are all higher than those of the CH_2 groups attached to the rigid PBA backbone. In addition, the different number of crystallized carbon atoms (N_c) indicates that the rigid polymer backbone cannot easily adjust its conformation to allow more CH_2 segments to pack into a crystal lattice. Similarly, the entropy changes also reflect the same tendency. On the other hand, this result further points out that the conformational states of the polymer backbone play an important role and determine the crystallization behavior of the alkyl side chains in comblike polymers.

Packing Mode of Side Alkyl Chains. The aforementioned main-chain effect on the side-chain crystal structure was deeply interpreted with respect to the molecular chain mobility and the conformational variations as studied by the FTIR technique. Figure 3 shows the CH_2 rocking vibrational bands of PEI18C and PBA18C in the heating process. It is a common knowledge that a doublet at 719/730 cm^{-1} is correlated to $\gamma_r(CH_2)$ of the orthorhombic packing form,[29−34] while a single band at 720 or 717 cm^{-1} is assigned to $\alpha_H(CH_2)$ of hexagonal or triclinic packing form,[29,31] respectively, and the band at 723 cm^{-1} corresponds to the amorphous part. As shown in Figure 3a, PEI18C exhibits double CH_2 rocking bands at 730 and 719 cm^{-1}, characteristic of the planar-zigzag *trans* conformation (orthorhombic phase),[35] while only single 720 cm^{-1} rocking band can be seen in PBA18C (Figure 3b). Obviously, the mobility and the conformational behavior of octadecyl side chains in these two comblike polymers are different. The restricting effect of the main-chain rigidity on the side-chain packing mode is more pronounced for the rigid PBA backbone than for the flexible PEI. The investigation of the CH_2 conformational band variations leads to the same conclusion: The alkyl side groups confined by the rigid PBA backbone form the irregular *trans−gauche* coexisting conformational band, while those at the flexible PEI backbone form the regular planar-zigzag *trans* conformational band. This result indicated that polymer backbones can not only affect the packing structure of alkyl side groups but also change their conformational states. With increasing temperature the blue shift and red shift of CH_2 rocking band can be observed for PEI18C and PBA18C, respectively, further confirming that the effect of PBA and PEI backbones on the mobility, conformational state, and phase behavior of the alkyl side chains is different. The detailed reason is currently studied by cryogenic high-resolution FTIR spectroscopy.

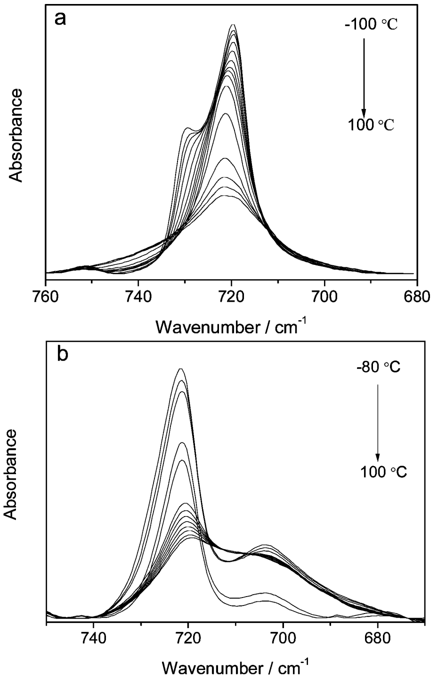

Figure 3. Rocking vibrational FTIR spectra of octadecyl side groups in PEI18C (a) and PBA18C (b) comblike polymers during the heating process.

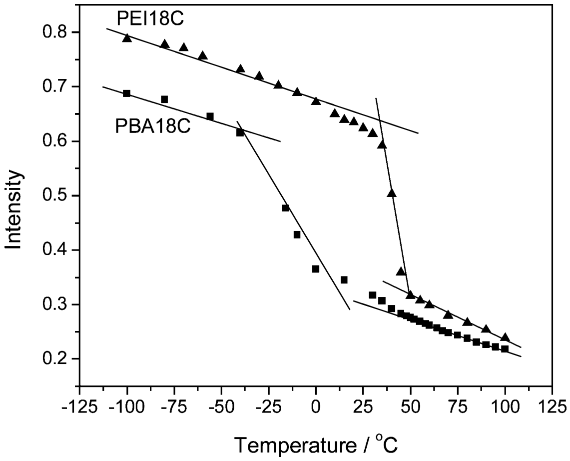

Figure 4. Variation of absorption intensity of the methylene rocking band in PEI18C and PBA18C comblike polymers with temperature.

In order to further understand the effect of polymer backbones on the phase behavior of alkyl side groups, the absorption intensity of the CH_2 rocking band as a function of temperature is depicted in Figure 4. It is obvious that the two comblike polymers show different temperature-dependent phase behaviors. With temperature increasing, in the phase transition region the methylene rocking band of PEI18C decreases faster, implying first-order phase transition; PBA18C, however, shows a slower phase transition behavior. Therefore, it can be deduced that the crystal structure and phase transition behavior of the alkyl side chains grafted onto the flexible polymer backbone are easily formed; i.e., the flexible backbone can adjust its conformation to adapt the ordered packing of alkyl side chains.

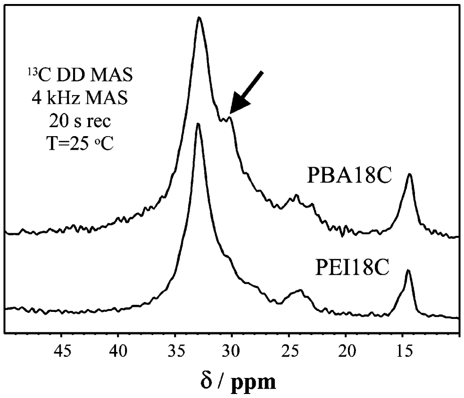

Figure 5. ^{13}C DD/MAS NMR spectra of PBA18C and PEI18C comblike polymers at room temperature.

Conformational Transition Behavior of Side Alkyl Chains by Solid-State NMR. Solid-state NMR spectroscopy is a powerful technique to elucidate phase structures and molecular chain motions of polymeric materials and was used here to understand the mobility of the molecular chains of the comblike polymers. The ^{13}C NMR chemical shifts of CH_2 in polyethylene and paraffins provide a good reference for the study of the phase structure variation in polymers containing alkyl side chains. 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.[35−39] To elucidate the effect of PBA and PEI backbones on the ordered state of alkyl side chains, ^{13}C DD/MAS NMR method was used to detect the variations in the crystal structures as formed by the alkyl side chains. It should be noted that the technique of ^{13}C DD/MAS NMR at short and intermediate recycle delay times is more sensitive to mobile components, while ^{13}C CP/MAS experiments enhance the intensity of rigid, proton-containing carbons with strong dipolar couplings.

Figure 5 shows the ^{13}C DD/MAS NMR spectra of the PEI18C and PBA18C side chains at room temperature. It was observed that PEI18C exhibits a relatively sharp resonance peak, centered at ca. 33 ppm, characteristic of crystal structure of the octadecyl side chains. On the contrary, PBA18C shows a much lower ordered structure by the existence of a shoulder at 30 ppm, corresponding to the amorphous phase formed by octadecyl chains. Therefore, it can be concluded that the rigidity of the main chain will influence the conformation state and crystal structure of the alkyl side chains confined between the polymer backbones. In order to obtain an in-depth understanding of the conformation variation of the octadecyl side chains with the different polymer backbones, ^{13}C CP/MAS NMR experiments at variable temperatures were performed. Figure 6 shows the expanded ^{13}C CP/MAS NMR spectra of the PEI18C and PBA18C side-chain signals as a function of the temperature. The peak assignments are labeled within the spectra.

The temperature-dependent solid-state NMR spectra were measured at a temperature range of 25−100 °C. Below the phase transition temperature (e.g., 40 °C for PEI18C), the peak corresponding to the inner methylenes (int-CH_2) in the *trans* conformation state appears at 33 ppm, while above the phase transition temperature, the CH_2 signals can be found at 30 ppm, as expected for a polymethylene chain undergoing a fast transition between the *trans* and *gauche* conformation.[40] Because of the applied ^{13}C CP/MAS technique, the intensity of the rigid (e.g., crystalline) components is enhanced, while the intensity of amorphous or molten parts is reduced. As illustrated in Figure 6, the variation of the chemical shifts of the CH_3, α-CH_2, and β-CH_2 can also be observed within the whole temperature range. With increasing temperature a second chemical shift of the α-CH_2 is detected and shifted by ca. 2 ppm for both polymers, while the resonance frequencies of the other two carbons (CH_3, β-CH_2) remain almost constant, when the alkyl side chains turn into a molten state. On the basis of the analysis of the chemical shift variation of different methylene groups, we can draw a conclusion that the confinement effect of main-chain rigidity on the side-chain crystallization behavior is present, especially for the inner methylene groups of the octadecyl side chains.

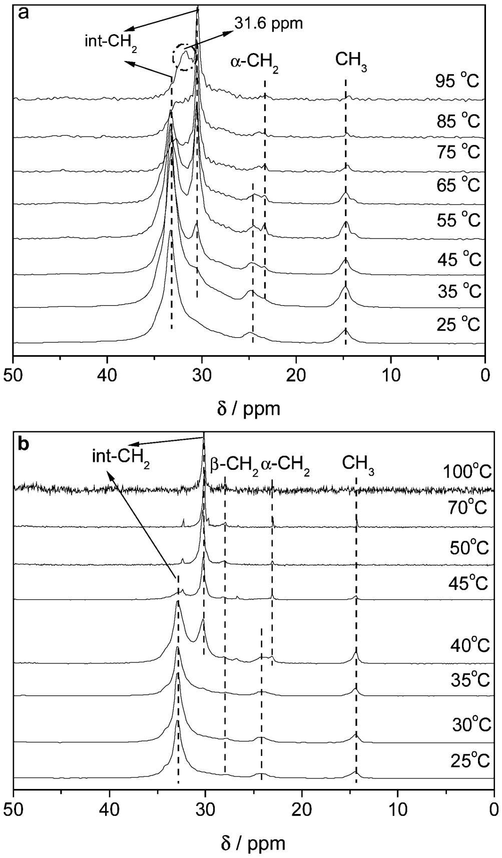

Figure 6. Expanded ^{13}C CP/MAS NMR spectra of the side-chain carbons of PBA18C (a) and PEI18C (b) as a function of temperature.

An interesting feature, observed with increasing temperature, is the new peak of a resonance frequency centered at 31.6 ppm (marked by the dashed circle in Figure 6a), which may result from the decreased mobility of the rigid poly(*p*-benzamide) backbone or the different crystallites with distribution of crystal size and perfection degree formed by CH_2 chain segments. A classical interpretation of this new peak was provided by Kitamaru,[41] who investigated the phase structure of polyethylene by solid-state NMR and found the component phases consist of three different phase structures: crystalline phase (33 or 34 ppm), crystalline−amorphous interphase (31.3 ppm), and isotropic−amorphous phase (31 ppm). So, the observed chemical shift at 31.6 ppm might indicate the existence of a crystalline−amorphous interphase between the side-chain crystal and the polymer main-chain structure. A question arises, why does PBA18C exhibit such a transitional behavior? For comparison, once above the phase transition temperature, the amorphous PEI main chain will lose the supporting anchors of the side-chain crystal and finally collapse at higher temperature; however, the rigid PBA backbone has better structural integrity at higher temperature, and thus, the side-chain mobility and melting process will also be strongly influenced by the PBA backbone. Therefore, the melting of crystallites formed by alkyl side groups will cover some certain temperature region because of crystalline distribution. Because of the applied ^{13}C CP/MAS technique with enhanced signals from crystalline, interphase, and disordered parts, the alkyl carbons that are immobilized by the rigid PBA backbone are detected at relative increased intensity. Therefore, a possible interphase chemical shift (31.6 ppm) can be observed in PBA18C NMR spectra. However, because of the aforementioned characterization methods (excluding NMR) are not sensitive to the molecular chain microregion mobility, no similar behavior can be seen. Therefore, in order to confirm this possible interphase transition, ^{13}C spin–lattice relaxation time T_{1C} measurements will be carried out in the future work.

It has to be pointed out that although our study has drawn some primary conclusions in the aspects of which factors influence the alkyl side-chain crystallization of two kinds of comblike polymers, this study is still at infancy and needs more attention. For alkyl side-chain crystallization, in fact, there are also many possible affecting factors, e.g., the different crystal structure, the alkylation degree, and the homogeneity of alkyl chain substitution along the polymer backbones, etc. From the present work, it can be confirmed by the multidisciplinary characterization techniques that the rigidity of the polymer backbone indeed has an obvious effect on the alkyl side chains crystallization behavior and on the conformation states. However, in order to make it clear why the packing mode and the mobility of the alkyl side chains are strongly affected by the rigidity of the polymer backbones, a series of investigations have to be performed, such as the motivation for the conformation variation, the crystalline structure transition of the alkyl side chains attached onto the polymer backbones, the effect of the length of alkyl side chains on the rigidity and packing modes of polymer main chains, etc.

Conclusions

The present study of PBA18C and PEI18C with the same length of *n*-alkyl side chains illustrates the effect of the polymer main chain on the phase transition and crystallization behavior of the side chains. Different crystal structures and packing modes of the octadecyl side chains can be observed in WAXD and FTIR spectra. Consequently, the polymer backbone conformations play an important role in the side chains' crystallization. The different crystallization numbers of alkyl side chain carbon atoms in PBA18C and PEI18C confirm the strong effect of the polymer main-chain structure. During the phase transition process, PEI18C exhibits a first-order transition behavior, while PBA18C shows a broad transition range like in the isotropic transition of liquid crystals. In addition, the ordered structure and the molecular chain mobility provide an explanation for the differences between the PBA and PEI backbones, and the new 31.6 ppm chemical shift illustrates that the rigid polymer backbone has a stronger effect on the side-chain crystallization and phase transition behavior.

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