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Crystalline structure and phase behavior of *N*-alkylated polypyrrole comb-like polymers

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We report the crystalline structure and phase behavior of a series of comb-like polymers (PPy-Cn), which were prepared *via N*-alkylation reactions between a pyrrole monomer and *n*-alkyl bromides (*n* = 18–26). Analysis by temperature-dependent X-ray diffraction and Fourier transform infrared spectroscopy (FTIR), as well as differential scanning calorimetry reveals that the crystal structure, thermal events and packing mode are affected by PPy backbones, which exhibit stronger rigidity than those of previously reported comb-like polymers. Remarkably, variable-temperature (VT)-FTIR proves the formation of orthorhombic phase at very low temperature, while VT-wide-angle X-ray diffraction only presents the hexagonal phase, illustrating that FTIR is a very sensitive tool for analyzing the micro-packing mode of molecular chains. The enhanced side-chain crystallizable carbon atoms indicate that PPy polymeric backbones play a negative role in the regular packing of nano-crystallites formed by alkyl groups.

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1. Introduction

Comb-like polymers have gained considerable attention in recent years due to their structural features and hierarchical self-assembly behavior, originating from the intermolecular interactions between the polymeric main-chains and the flexible alkyl side-chains.¹ The physical properties of comb-like polymers are strongly affected by the rigidity of polymeric main-chains and the length of flexible side-chains.^{2–9} Therefore, understanding the interesting structural state of comblike polymers is very important for designing topological polymers and strengthening knowledge of polymer crystallization.

Comb-like polymers present interesting crystals and phase structures, and they exhibit dependence upon the side-chain length and polymer backbones. For flexible backbones, 8 crystallizable carbon atoms are required to form the hexagonal phase $(\alpha_{\rm H})$,^{10,11} while for the rigid ones 12 or more carbon atoms are the minimum. Turner-Jones reported orthorhombic ($\beta_{\rm O}$) phase structures in poly(α -olefin)s,¹² while for poly(*n*-alkyl methacrylates),¹³ aromatic polyesters with aliphatic side-chains,^{7,14} *N*-alkylated polyaniline^{15–17} and poly(3-alkyl thiophene),^{2,18,19} $\alpha_{\rm H}$ phase was the only phase structure. In our previous studies of *N*-alkylated polyethyleneimine (PEI(*n*)Cs, $12 \le n \le 26$),^{9,11,20–24} the packing mode of pended alkyl groups exhibiting the dependence upon side-chain length is proven. For example, PEI16C and PEI18C take $\alpha_{\rm H}$ and $\beta_{\rm O}$ phase, respectively, while for PEI(*n*)Cs with $n \geq 20$ the coexistence phase of $\beta_{\rm O}$ and $\alpha_{\rm H}$ is found. These results indicate that the nanocrystal structure of comb-like polymers, *i.e.*, $\alpha_{\rm H}$, $\beta_{\rm O}$ or the two phases coexisting, is dependent on the confinement alkyl side groups and the polymeric backbones. Although some studies have discovered the ordered structure composed by alkyl groups, understanding the interaction of the polymeric backbone with side-chain crystallization is still needed to clarify the nanoconfined crystallization behavior of side-chains.

Polypyrrole (PPy) is an amazing polymer with high conductivity and excellent chemical stability. To improve the processability, chemical modifications have been explored. Hamaide prepared *N*-substituted and *N*-oxyalkyl pyrrole under solid triphase transfer catalysis conditions, and a low alkylation degree was found.²⁵ Sant'Ana *et al.* synthesized 1-dodecyl pyrrole derivative through alkylation reaction *via* charge-transfer catalysis.²⁶ To the best of our knowledge, however, information on *N*-alkylated PPy containing the variable side-chain length (*n*) from *n* = 18 to 26 is still not clear, and the phase structure and crystallization behavior of *N*-alkylated PPy derivatives also needs to be further investigated.

In this paper, a series of *N*-alkylated PPy comb-like polymers (PPy-Cn, n = 18, 20, 22, 26) are prepared through *N*-alkylated technique, as reported in our previous studies. The phase behavior and crystalline structure of PPy-C*n* comb-like polymers is deeply characterized by differential scanning calorimertry (DSC), variable-temperature wide-angle X-ray diffraction (VT-WAXD) and Fourier transform infrared



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spectroscopy (VT-FTIR). In particular, the ordered structure and thermal behavior of PPy-C*n* comb-like polymers are analyzed and compared with our previous studies in terms of the molecular packing and phase transition process.

2. Experimental section

2.1 Materials

Pyrrole (Py) (\geq 98%) was purchased from Aldrich and used after refining. A series of *n*-alkyl bromides, (*n* = 18, 20, 22, 26) were obtained from TCI and were used as received. Sodium hydride (NaH), dimethyl sulfoxide (DMSO), ferric chloride (FeCl₃), CH₃OH and chloroform were purchased from Tianjin Sailboat Chemical Reagent Co., Ltd and used as received.

2.2 Preparation of N-alkylated PPy-Cn comb-like polymers

For the synthesis of PPy-C*n* comb-like polymers, two steps are proceeded based on our studies.^{10,11,27–29} Firstly, the monomer Py was substituted by *n*-alkyl bromide in a homogenous solution. 0.5 g NaH was dissolved in 50 ml anhydrous DMSO and the suspension was stirred at 70 °C for 2 h under nitrogen gas. 9 mmol Py was added, and the system was continuously stirred for 4 h, and then 9 mmol *n*-alkyl bromide was added under stirring. The reaction was kept for another 5 h under stirring and N₂ gas atmosphere. After the reaction was finished, NaBr was filtered off, and the solvent was removed. The Py-C*n* derivatives were rinsed alternatively with deionized water and CH₃OH three times, and finally dried under vacuum.

Secondly, PPy-C*n* comb-like polymers were synthesized under the catalysis of $FeCl_3$ in chloroform solution at 0 °C for 24 h. After that, the solution was dropped and washed with CH₃OH until no light green solid appeared. The final PPy-C*n* comb-like polymers were dried in a vacuum-oven for 3 h before use. Scheme 1 presents the detailed preparation process of PPy-C*n* comb-like polymers.

2.3 Characterization

Nuclear magnetic resonance spectroscopy. Nuclear magnetic resonance (NMR) measurements were carried out on a Bruker DMX 300 MHz NMR spectrometer at 25 °C. Deuterium chloroform was used as the solvent and tetramethylsilane as an internal reference.

Differential scanning calorimetry (DSC). A TA differential scanning calorimeter Q2000, calibrated with indium, was used to study the thermal behavior of PPy-Cn. Specimens of



 $\mathbf{R} = -\mathbf{C}_{18}\mathbf{H}_{37}, \ -\mathbf{C}_{20}\mathbf{H}_{41}, \ -\mathbf{C}_{22}\mathbf{H}_{45}, \ -\mathbf{C}_{26}\mathbf{H}_{53}$

Scheme 1 Synthesis process of *N*-alkylated polypyrrole comb-like polymers.

3-5 mg were encapsulated in aluminum pans and firstly heated from -30 to 100 °C and kept at 100 °C for 10 min, subsequently the samples were cooled to -30 °C and kept for 10 min, and finally the samples were heated again from -30 to 100 °C. The DSC thermogram in the second heating process was recorded, and the heating/cooling rate was 10 °C min⁻¹.

Variable-temperature wide-angle X-ray diffraction. WAXD measurements were performed on a Rigaku/max-2500 X-ray diffractometer over the temperature range of -90 to 100 °C, using the Cu K α radiation of 1.542 Å.

Variable-temperature Fourier transform infrared spectroscopy. The FTIR measurements were performed on a Bruker Equinox-55 spectrometer equipped with a temperaturevariable cell, and the spectra were processed with Bruker OPUS program. The cell was kept in a vacuum by an oil pump, and liquid nitrogen was used as the coolant. A resolution of 2 cm⁻¹ was chosen and 32 scans were run. Infrared spectra were recorded from -70 and 100 °C. At each temperature point, the samples were equilibrated for 5–8 min before measurements.

3. Results and discussion

¹H NMR is used to analyze the structure of Py-C*n* monomer and the related PPy-C*n* derivatives, and here Py-C22 and PPy-C22 are given as an example. As shown in Fig. 1a, the peaks at 6.65 and 6.13 ppm are characteristic of H atoms at the 2,5-position and 3,4-position of the Py ring, respectively. Peaks of side alkyl chains are located at 1.75, 1.56, 1.25, 0.88 ppm, respectively,²⁶ while H atoms of $-NCH_2$ - are located at 3.88 ppm. The substitution degree of C22 alkyl groups on the Py ring is calculated according to the area ratio of H atoms of the Py-ring and CH₂ connected by the N atom of the Py-ring. This result demonstrates the successful substitution reaction of C22 side-chains on the N site of Py. Thereafter, the Py-C22 monomer is used to prepare the PPy-C22 derivative, and ¹H NMR spectroscopy is given in Fig. 1b, indicating that the PPy-C22 comb-like polymer has been successfully prepared.

Considering the influence of alkyl side-chains on the crystallization behaviour of comb-like polymers, as reported in previous studies,^{1,30} the thermal property of PPy-Cn comblike polymers is investigated by DSC, and the thermal events also are compared with the previously reported comb-like polymers. Fig. 2 presents the DSC curves of PPy-Cn comb-like polymers in the heating and cooling process. From these curves, the obvious endothermic and exothermic process appears, originating from the contribution of side-chain crystals.^{31–33} With increasing side-chain length from 18 to 26, the melting (T_m) and freezing (T_c) temperature exhibit a linear change, changing from 19.8 to 70.0 °C and from 13.3 to 61.0 °C, respectively. Similarly, the melting enthalpy also shows a linear increment tendency, followed by an increase from 9.9 to 38.2 kJ mol⁻¹, proving that the grafted side alkyl chains formed the ordered crystal structures surrounded by PPy backbones. To further analyze the ordered packing mode



Fig. 1 $\,^1\text{H}$ NMR spectra of Py-C22 (a) and PPy-C22 (b) comb-like polymer.

of side-chain crystals, the melt enthalpy of PPy-Cn vs. the carbon number of the alkyl side-chain is plotted in Fig. 3 according to eqn (1), where k is the contribution of each added CH₂ group to enthalpy, and $\Delta H_{m,e}$ is a constant reflecting the contribution of chain end to enthalpy.^{10,34}

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

Through the fitted result of Fig. 3, the slope *k* is obtained and its result is 3.56 kJ mol⁻¹·CH₂. According to previous studies, it is well-known that the slope *k* reflects the crystal structure of side alkyl groups. Usually, if the *k* value is around 3.99 or 4.2 kJ mol⁻¹·CH₂, the alkyl side groups constitute the rhombic or triclinic phase, respectively. However, if the *k* value is *ca*. 3.07 kJ mol⁻¹·CH₂, hexagonal phase is the major form.³⁴ For this estimated result, PPy-C*n* comblike polymers should pack into a hexagonal phase, which is similar to other comb-like polymers with long alkyl sidechains, such as poly(*n*-alkyl methacrylate),^{30,35} *N*-alkylated poly(*p*-benzamide),¹⁰ *N*-alkylated copolyamides,³⁶ and poly(*n*-alkyl itaconate).³⁷

Additionally, it is well-known that only when the length of the side alkyl groups is beyond a certain value does the sidechain crystallization behavior appear. It is worth noting that



Fig. 2 DSC curves of PPy-Cn comb-like polymers at a scanning rate of 10 °C min⁻¹ in the heating process (a) and cooling process (b).



Fig. 3 Melt enthalpy of PPy-C*n vs.* the carbon number of the alkyl side-chain. The " \blacksquare " values are experimental data, and the red line is a linear fit with a slope of 3.56 kJ mol⁻¹ per CH₂ group.

only the part of side-chains away from the polymeric backbone, participate in the formation of crystals, and the size of side-chain crystals is dependent upon the length of the sidechains. To obtain the crystalline degree of side-chain crystals and the crystallizable carbon atoms per side-chain, eqn (2) and (3), as described in previous studies, are used.¹¹ The number of crystallizable CH₂ groups (N_c) and the crystallinity (X_c) of PPy-C*n* comb-like polymers are listed in Table 1.

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Table 1 Calorimetric data for PPy-Cn comb-like polymers

Sample	$T_{\rm m}$, °C	$T_{\rm c}$, °C	$\Delta H_{\rm m}$, kJ mol ⁻¹	<i>X</i> _c , %	N _c
PPy-C18	19.8	13.3	9.9	11.9	2.7
PPy-C20	45.1	33.4	17.1	18.8	4.6
PPy-C22	55.3	46.0	25.7	26.3	7.0
PPy-C26	70.0	61.0	38.2	34.0	10.4

$$N_{\rm c} = \Delta H_{\rm m}/k \tag{2}$$

$$X_{\rm c} = (N_{\rm c} \times 14.026) / M_{\rm unit} \tag{3}$$

As shown in Table 1, N_c increases from 2.7 to 10.4 and X_c increases from 11.9% to 34.0% with *n* changing from 18 to 26. It is concluded that only when the carbon atoms of sidechains is over 16 does the side-chain crystallization behavior for PPy-Cn comb-like polymers appear. To further understand the thermal properties of comb-like polymers, the relationship of $T_{\rm m}$ against the carbon atom (n) per side-chain in various comb-like polymers is plotted in Fig. 4. As shown in Fig. 4, poly(*n*-alkyl methacrylate) (PnAMA),³⁸ PEI(n)C,¹¹ poly (styrene-co-maleic anhydride)-graft-1-alcohol (SMA-g-CnOH),³¹ and PPy-Cn exhibit higher T_m than those of n-alkanes, while for N-alkylated poly(p-benzamide)s (PBA(n)C),¹⁰ the $T_{\rm m}$ is lower than that of *n*-alkanes.³⁹ Usually, *n*-alkane takes the layer-by-layer stacking structure, while for comb-like polymers, hexagonal phase is the major form. Such $T_{\rm m}$ changes should be ascribed to the different stacking manner of alkyl groups and the influence of polymer backbones. Note that, rigid PPy and PBA backbones have an obvious influence on $T_{\rm m}$ of confined side alkyl groups, indicating that the mobility of alkyl chains is different from that of flexible backbones. The PPy-Cn series requires more carbon atoms to realize side-chain crystallization behaviour than that of PBA(n)C, *i.e.*, 2.7 for PPy-18 and 5.7 for PBA18C, indicating that the PPy backbone is more rigid than that of PBA. Interestingly, however, the PPy-Cn series exhibits the higher $T_{\rm m}$ and $T_{\rm c}$ than that of PBA(n)C, as shown in Fig. 4. The explanation is not clear, and the reason needs to be further investigated in the future.



Fig. 4 Melting temperature *vs.* carbon atoms of the side-chain in various comb-like polymers and *n*-alkane.

The DSC results indicate that only the part of side-chains away from the PPy backbone takes part in the formation of side-chain crystals. Thus, XRD is used to analyze the crystalline structures of side-chain crystals. Fig. 5 gives the XRD patterns of PPy and PPy-*Cn* comb-like polymers at room temperature. PPy shows a weak halo peak at 25.1°, while PPy-*Cn* derivatives present one single sharp diffraction peak at 21.4° (d = 4.2 Å), characteristic of $\alpha_{\rm H}$ phase according to the previous studies.¹³ Besides, an amorphous halo in PPy-C18 also appears, further indicating its low crystallinity which is in good agreement with the DSC results.⁴⁰ The crystalline structure in PPy-*Cn* comb-like polymers should originate from the contribution of side alkyl groups because bulk PPy appears as a weak peak at 25.1°.

To further clarify the changes of side-chain crystals, VT-WAXD is utilized to detect the phase transition behavior (Fig. 6). With temperature increasing from –90 to 60 °C, the intensity of the diffraction peak at 21.4° gradually decreases, and once the temperature is above 80 °C this diffraction peak disappears. Similarly, the peak position 21.4° also exhibits the same variation with the intensity. The peak position almost keeps constant at 21.4° before 60 °C, and when temperature is above 80 °C the diffraction peak shifts to 19.6° (d = 4.6 Å),



Fig. 5 XRD curves of PPy and PPy-C*n* comb-like polymers at room temperature.



Fig. 6 VT-WAXD curves of PPy-C26 with temperature changing from –90 to 100 $^\circ\text{C}.$

characteristic of the amorphous state. The temperature transition range is in good agreement with that of the DSC result, indicating that the melting process is attributed to the phase transition from $\alpha_{\rm H}$ phase to amorphous state of the sidechain crystals.¹⁰ It is worth noting that PPy-C26 shows the asymmetric diffraction peak at 21.4° at low temperature. After the curve-fitting of -90 °C diffraction peak, it further shows a shoulder peak at 23.4° (d = 3.8 Å) close to the peak at 21.4°. This is possibly influenced by the low temperature effect, and then contributes to the regular packing of alkyl groups. Similarly, PEI18C also gives the same behavior, and this shoulder peak is assigned to $\beta_{\rm O}$ packing.¹¹

From the above XRD results, it is found that the crystallization behavior of the confined side alkyl groups in PPy-C26 is greatly decreased due to the limited mobility afforded by rigid PPy.

FTIR is a powerful tool to detect microstructural information and the packing mode of molecular chains from a microscopic viewpoint. As a kind of side-chain crystallization polymer, PPy-Cn comb-like polymers exhibit the obvious phase transition process with temperature change, especially at low temperature. Here, taking PPy-C26 comb-like polymer as an example, we analyze the phase transition process and the relevant packing mode of side alkyl groups distributed along the PPy backbone. Fig. 7 presents the changes of rocking band $(\gamma_r(CH_2))$ of CH₂ groups in PPy-C26 comb-like polymer with temperature during the heating and cooling process. Information on the packing mode of CH₂ sequences can be obtained from *n*-alkanes and our previous results on PEI(*n*)Cs and PBA(*n*)Cs series comb-like polymers.^{9–11,20,22,23,41,42} A doublet at 719/730 cm⁻¹ is correlated to γ_r (CH₂) of β_O packing, while a single band at 720 cm⁻¹ is attributed to $\alpha_{\rm H}$ packing. As shown in Fig. 7a, it is found that the obvious double bands at 719/730 cm⁻¹, characteristic of β_0 packing of CH₂ chains, appear below 0 °C. With temperature increasing from -40 to 20 °C, 730 cm⁻¹ band gradually disappears followed by the decreased absorption intensity, indicating that the β_0 packing has been transformed into $\alpha_{\rm H}$ phase.^{22,23,27} With temperature further increasing to 100 °C, the single 719 cm⁻¹ band almost keeps constant until the phase transition occurs at 70 °C, and then shifts to around ~720 cm⁻¹, characteristic of the crystalline C26 alkyl groups entering into the amorphous state.²¹ Similarly, the reverse band shift and the phase transition process are also found in the cooling process (Fig. 7b), demonstrating that the phase transition from $\beta_{\rm O}$ - $\alpha_{\rm H}$ phase to the amorphous state is reversible with temperature. The similar phase transition process is also observed in other series of comb-like polymers, such as PEI(n)C, ^{22,23} PBA(n)C, ⁹ CS(n)Cs, ²⁷ *etc.* This proves that FTIR is a sensitive technique for detecting the microstructural changes and phase behavior of the confined side alkyl groups. To clearly understand the phase transition behavior of C26 side alkyl groups, the absorption intensity of 719 cm⁻¹ band (Fig. 8) is plotted as a function of temperature during the heating and cooling process. As shown in Fig. 8, the intensity of the 719 cm⁻¹ band gradually decreases with increasing temperature, and the temperature transition range appears between 40



Fig. 7 Rocking bands of methylene group of PPy-C26 vs. temperature during the heating (a), and cooling (b) process.



Fig. 8 The changes of the absorption intensity of rocking band with temperature.

and 70 °C, corresponding to $\alpha_{\rm H}$ -melt phase transition process, as proved by the VT-WAXD and DSC results.

The phase transition from $\alpha_{\rm H}$ phase to amorphous state, is directly observed in XRD and DSC result; while the FTIR result, shows transition from $\beta_{\rm O}$ - $\alpha_{\rm H}$ phase and then to the amorphous state. It should be noted that the transition behavior between WAXD and FTIR exhibits inconsistency, which could be attributed to the experiments not being carried out on the same instrument. Additionally, it can be concluded that FTIR is a sensitive tool to analyze the crystal packing of molecular chains in the aspect of molecular viewpoint. It is also worthy to note that PPy main chains are more rigid than our previously reported polymer backbones in comb-like polymers, such as PBA, chitosan and PPTA, *etc.* PPy-C*n* comb-like polymers show lower crystallinity and smaller crystallizable carbon atoms than that of other series of comb-like polymers, however, the appearance of regular packing of the orthorhombic phase at low temperature makes the role of the polymer backbone complicated. The information is not clear now, and further characterizations are still needed.

Conclusions

In summary, *N*-alkylated polypyrrole (PPy-C*n*) comb-like polymers with the carbon number of alkyl side-chains ranging from 18 to 26 exhibit typical side-chains crystallization behavior, as observed in previously reported comb-like polymers. PPy-C*n* comb-like polymers show the obvious crystalline structure, characteristic of β_0 and α_H phase. Phase transition from $\beta_0-\alpha_H$ phase to amorphous state is demonstrated by FTIR, while XRD only proves the transformation from α_H phase to amorphous state in PPy-C26. This result indicates that FTIR is a sensitive tool to analyze the microstructural packing of confined alkyl side groups. Furthermore, the phase transition and crystallinity of PPy-C*n* comb-like polymers is different from that of previously reported comb-like polymers like PBA(*n*)Cs, CS(*n*)Cs and PPTA(*n*)Cs, which is attributed to the rigid conjugated PPy backbone.

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