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Hydrogen bonding effects on the conformational changes of polyglutamates containing long flexible side chains

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Abstract

The FT-IR spectra for three polyglutamates containing different side chains, poly(γ-methyl α, L-glutamate) (PMLG), poly(γ-hexyl α, L-glutamate) (PHLG), and poly(γ-stearyl α, L-glutamate) (PSLG), were measured and analyzed. Experimental data show that longer side chains induce weaker hydrogen bonds between the carbonyl groups and the amide linkages of the α-helical backbone. Simulated infrared spectra strongly support the infrared spectra with remarkable accuracy. Variable temperature FT-IR measurements on PHLG and PSLG were also performed to examine the effect of temperature on the conformational behavior of the side chains. In the case of PHLG, no perceptible conformational change has been found with increasing temperature. On the other hand, the changes of the characteristic vibrational bands have been found for the infrared spectra of PSLG after the temperature of phase transition. The relative broadness of several bands over 60°C suggests that the increased mobility of the long side chains affects the conformation of the α-helical backbone.

Keywords: Polyglutamate; Hydrogen bonding; FT-IR

1. Introduction

Recently, polyglutamates containing long flexible side chains have attracted considerable attention due to their interesting physicochemical properties [1,2]. Polyglutamates are known as promising polymers for their applications in liquid crystalline materials as well as to photofunctional devices [3–7]. Polyglutamates consist of two structural elements: an α-helical backbone of the polymer main chain (rod) and a skin of long flexible side chains (hair) [8]. The former gives the macromolecular structure rigidity, and the latter ensures solubility and processability of the polymer. Since this characteristic hairy-rod property enables uniform dispersions of the polymers without aggregation, polyglutamates have been widely used to construct self-assembled monolayers on solid substrates [9–17].

In order to understand clearly the self-assembling capability of polyglutamates on a surface, the conformational property of the polymer should be elucidated. Polyglutamate containing long side chains is known to exist as a rigid α-helical structure, because the backbone is stabilized by the N–H···O=C hydrogen bonds [18,19]. This rigid α-helical conformation restrains the segmental motion of the polymer main chains, and the layered structure is kept stable. Thus, the intramolecular hydrogen bonds in the α-helical backbone play a key role in determining the conformational rigidity of the polymer. On the other hand, the side chains of polyglutamates are introduced to increase the solubility as well as to reduce the melting temperature of the poorly soluble rod-like polymer [20,21]. To our knowledge, however, very little is known about how the side chains of polyglutamates affect the hydrogen-bonding property of the α-helical backbone.

In the present work, we have measured and analyzed the infrared spectra for three polyglutamates containing different side chains, poly(γ-methyl α, L-glutamate) (PMLG), poly(γ-hexyl α, L-glutamate) (PHLG), and poly(γ-stearyl α, L-glutamate) (PSLG) in order to understand better the chain length effect on the conformation of the α-helical backbone. Fig. 1 shows the molecular structure of PMLG containing the shortest methyl side chain among three different side chain polymers. The spectroscopic studies for those three polymers are expected to be crucial in elucidating the structure–property relationships of polyglutamates. Theoretical simulations for the three different

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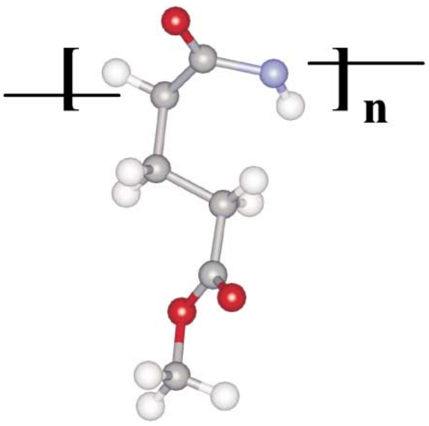

Fig. 1. Molecular structure of PMLG.

polymers are also performed. These calculations provide a very useful tool in explaining a theoretical picture of the conformational properties and vibrational spectra of the polymers.

In addition to the side chain effects on the hydrogen-bonding strength of the α-helical backbone, the thermal stability above room temperature is very important for device applications. Due to the increased mobility of the hairy side chain at higher temperature, the conformational property of the rod-like backbone will be changed. In this point of view, variable temperature FT-IR measurements have been carried out on PHLG and PSLG to examine the temperature effect on the conformation of the polyglutamate molecule.

It is the aim of this paper to elucidate the side chain and temperature effects on the conformational behavior of polyglutamates containing different side chains using FT-IR spectroscopy. As support for the analysis of the experimental infrared spectra, we also present the main results of a theoretical study performed on three polyglutamates.

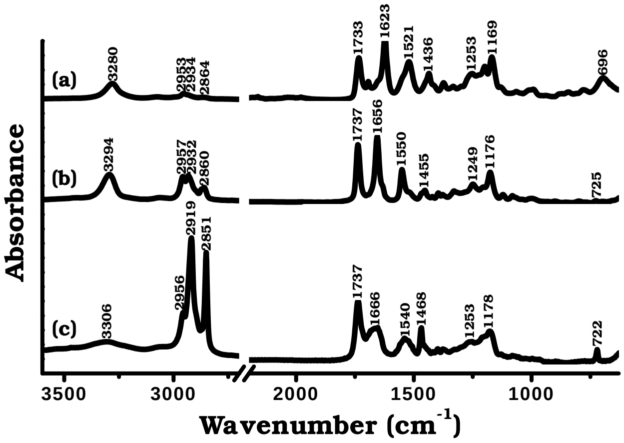

Fig. 2. FT-IR spectra recorded at room temperature in the 700–3600 cm^{-1} region: (a) PMLG; (b) PHLG; (c) PSLG.

2. Experiment and computational details

PSLG was synthesized by Professor P.S. Russo at Louisiana State University. PMLG and PHLG were purchased from Sigma Chemical Co., and used without further purification.

Mid-infrared spectra were recorded on a Bio-Rad FTS-6000 interferrometer with a cryogenic MCT detector. The spectra recorded at elevated temperatures were obtained with a Graseby–Specac heat controller cell, which has a reported accuracy of ±0.1°C. The sample was sandwiched between two KBr plates located in the electrical heating jacket connected to a temperature controller. Special attention was paid to ensure that all the samples examined were sufficiently thin to be within the absorption range where the Beer–Lambert law is obeyed. A heating rate of 5°C min^{-1} was used. All the spectra were recorded at a resolution of 4 cm^{-1}. The sample chamber was continuously purged with nitrogen gas to remove the water vapor absorption.

Molecular models for PMLG, PHLG and PSLG were constructed using eleven glutamate residues in a standard α-helical conformation. The molecular geometry of each substituted polyglutamate was fully optimized using the AM1 method. All the calculations were performed using the GAUSSIAN 98 program package [22] implemented on an alpha-cluster computer system. The vibrational frequencies and infrared intensities were calculated using the B3LYP method for experimental comparison purposes. The GAUSSVIEW program was also used to visualize the vibrational modes to assist in the assignment of the spectra.

3. Results and discussion

3.1. Chain length dependence on the conformation of the α-helical backbone

The infrared spectra of the three polyglutamates containing different side chains have been measured and analyzed in order to understand the side chain effect on the conformation of the α-helical backbone. Fig. 2 shows the infrared spectra of PMLG, PHLG and PSLG in the 700–3600 cm^{-1} region. The characteristic infrared bands of the three polymers are summarized in Table 1. The infrared bands occurring between 2800 and 3000 cm^{-1} are associated with the symmetric and asymmetric C–H stretching modes of the side chain CH_2 groups. The strong infrared bands between 1730 and 1740 cm^{-1} are assigned to the C=O stretching modes of the side chain COOR groups. These bands do not show any large frequency shifts with increasing alkyl chain length since the C=O group of the side chain does not exist in a hydrogen-bonding environment. The infrared bands in the 1160–1180 and 690–730 cm^{-1} regions are assigned to the CH_2 wag and CH_2 rock modes, respectively. Three characteristic amide bands are observed in the 1620–1670 cm^{-1} (amide I), 1520–1550 cm^{-1} (amide II), and

Table 1
Characteristic vibrational frequencies and bond lengths for C=O and N–H bonds of PMLG, PHLG and PSLG

Vibrational description	PMLG		PHLG		PSLG	
	Observed	Calculated[a]	Observed	Calculated[a]	Observed	Calculated[a]
N–H stretch	3280	3248	3294	3368	3306	3377
Asymmetric CH_2 stretch	2934	3001	2932	3010	2919	3010
Symmetric CH_2 stretch	2864	2889	2860	2891	2851	2878
C=O stretch	1733	1740	1737	1736	1737	1750
Amide I mode	1623	1680	1656	1691	1666	1745
Amide II mode	1521	1544	1550	1576	1540	1557
CH_2 deformation	1436	1458	1455	1471	1468	1482
Amide III mode	1253	1267	1249	1275	1253	1285
CH_2 wag	1169	1114	1176	1119	1178	1108
CH_2 rock	696	707	725	747	722	747
Bond lengths						
C=O bond		1.2512		1.2420		1.2360
N–H bond		1.0304		1.0204		0.9984
N–H···O=C hydrogen bond		2.1082		2.3633		2.5830

[a] B3LYP/6-31G(d)//AM1 level; frequencies were scaled by 0.9614.

1245–1255 cm^{-1} (amide III) regions for the three polyglutamates, and all of which show the typical α-helical conformations.

The infrared regions of particular interest are the N–H stretching from 3200 to 3400 cm^{-1} and the amide I from 1600 to 1700 cm^{-1}. This is because the spectral features in these regions are not only sensitive to the hydrogen-bonding strength of the α-helical backbone but also dependent on the side chain length [23–25]. The N–H stretching bands at 3280, 3294, and 3306 cm^{-1} for PMLG, PHLG and PSLG, respectively, indicate that each N–H group participates in a different hydrogen-bonding environment. In other words, weaker hydrogen bonds are formed by increasing the side chain length, and the hydrogen-bonded N–H stretching band shifts to higher frequency. Unlike the isolated N–H stretching mode, the amide I mode is comprised of contributions of the C=O stretching, the C–N stretching and the C–C–N deformation modes. Among these vibrational modes, however, the contribution of the C=O stretching mode is about 80% [26–28]. Thus, the amide I mode is conformationally sensitive to the hydrogen-bonding strength caused by the side chain length. As shown in Fig. 2, the amide I band is shifted in frequency from 1623 (PMLG) to 1666 (PSLG) cm^{-1} with increasing side chain length. This observation also reveals that weaker hydrogen bonds are formed by increasing the length of alkyl side chain.

The calculated vibrational frequencies for PMLG, PHLG and PSLG are also compared with the experimental data in Table 1. A full geometry optimization was performed at the AM1 level to find a minimum energy structure, and then the normal mode calculations in Cartesian coordinates were performed at the B3LYP/6-31G(d) level for each polymer molecule. For a better comparison of the calculated frequencies with the observed frequencies, the calculated frequencies are uniformly scaled [29]. As shown in Table 1, all the calculated vibrational frequencies show a reasonable agreement with the observed ones. In particular, the vibrational bands for both the N–H stretching and amide I bands appear to be shifted to higher frequencies with increasing side chain length. Table 1 also lists the N–H and C=O bond lengths optimized at the AM1 level, for PMLG, PHLG and PSLG. The simulated data reveal that the N–H and C=O bonds are shortened by increasing the side chain length. On the contrary, the hydrogen bond is lengthened as the side chain length increases. The results indicate that the long side chain induces the reduction of the rigid rod-like property due to the weaker hydrogen bonds between the carbonyl group and the amide linkages of the α-helical backbone.

The optimized geometrical structures of PMLG, PHLG and PSLG at the AM1 level are shown in Fig. 3. In order to obtain a reasonable α-helical model, eleven repeating residues have been used for each polymer. The calculated hydrogen-bond lengths in the α-helical backbones are 2.1082, 2.3633 and 2.5830 Å for PMLG, PHLG and PSLG, respectively.

3.2. Temperature effect on the conformations of PHLG and PSLG

Variable temperature FT-IR measurements were performed on PHLG and PSLG to examine the effect of temperature on the conformational behavior of the side chains. In the case of PHLG, there does not appear to be any frequency shift or intensity change over the entire temperature range. This means that no perceptible conformational change has been found with increasing temperature.

On the other hand, the infrared spectrum of PSLG

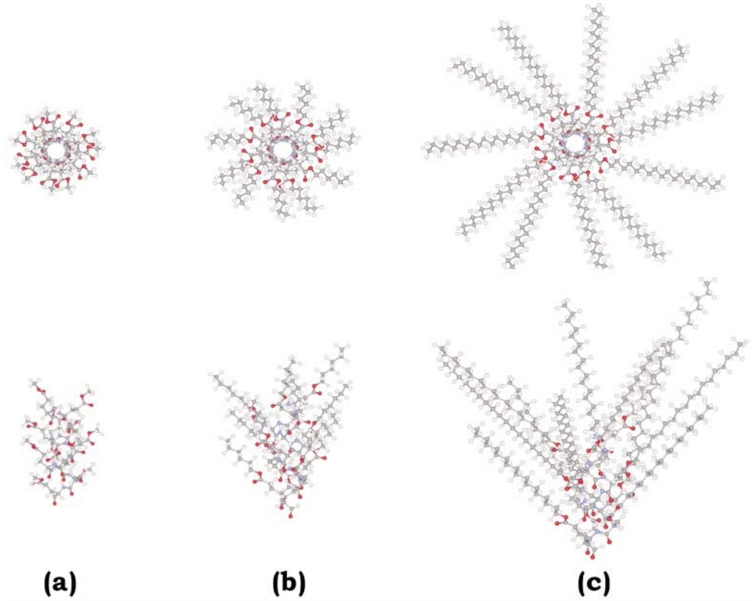

Fig. 3. Optimized geometrical structures of: (a) PMLG, (b) PHLG, and (c) PSLG; upper: top view, lower: side view.

strongly depends on temperature. Fig. 4 shows the variable temperature infrared spectra of PSLG as a function of increasing temperature. It is important to notice that the transition from the crystalline to the amorphous phase is signified by the band shape changes of some vibrational modes. Fig. 5 shows the FT-IR spectra of PSLG, corresponding to: (a) CH_2 stretching, (b) amide I, (c) CH_2 deformation, (d) CH_2 rock, (e) N–H stretching and (f) amide II modes at 26 and 80°C. For instance, Fig. 5(a) corresponds to the change of the CH_2 vibrational modes for the side chain. PSLG has a crystalline property from 26 to 60°C, and this is reflected in the infrared spectrum by the presence of the intensely sharp CH_2 bands that are characteristic of the preferred ordered conformation. At 60°C, above the transition temperature of PSLG, the infrared spectrum is characterized by the presence of the relatively broad CH_2 bands that are typical of the amorphous state. The transition temperature of 60°C was also identified by a differential scanning calorimeter experiment.

In addition to the spectral changes of the CH_2 bands, a further pronounced variation of the amide I band was found in the amorphous state. As shown in Fig. 5(b), a broad amide I band, centered at $1666\ cm^{-1}$, predominantly splits into two bands, at 1684 and $1630\ cm^{-1}$, above the transition temperature. We speculate that this band splitting is due to the distortion of the α-helical backbone related to the C=O, C–N and C–C–N groups. Such a band splitting and intensity change in the amide I region should be ascribed to the increased mobility of the long alkyl side chains above 60°C. In the amorphous state, the mobility of the long side chains is faster, and the increased mobility strongly has an effect on the conformational change of the α-helical backbone. However, any band shift or intensity change for the amide I band was not found below 60°C. This is because the mobility of the alkyl side chains is restrained due to its ordered crystalline property at those temperatures.

The N–H stretching mode of PSLG in Fig. 5(e) spans a range of about $3200–3500\ cm^{-1}$. Our normal mode analysis shows that this mode is composed solely of the N–H stretching vibration. Accordingly, the vibrational frequency for this mode strongly depends on the strength of N–H···O=C hydrogen bond in the backbone. After the phase transition at 60°C, the band maximum of the hydrogen-bonded N–H band shifts to slightly higher frequency and there is a small decrease in band intensity. This means that the increased mobility of long side chain weakens the hydrogen bonding intensity and relatively strengthens the force field of N–H bond. On the other hand, the amide II mode in Fig. 5(f) does not display the same features with the N–H stretching mode. The amide II band is known to

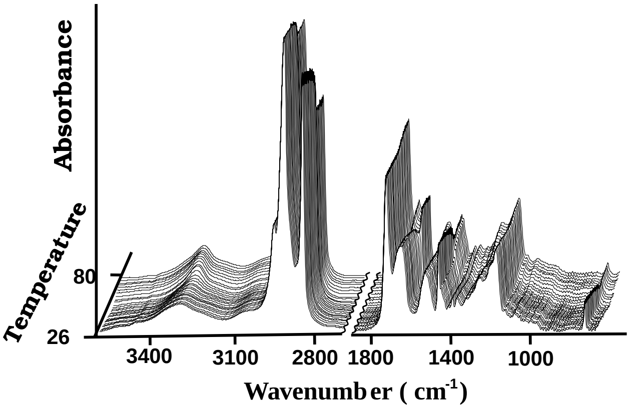

Fig. 4. FT-IR spectra of PSLG recorded between 26 and 80°C in the 700–$3600\ cm^{-1}$ region.

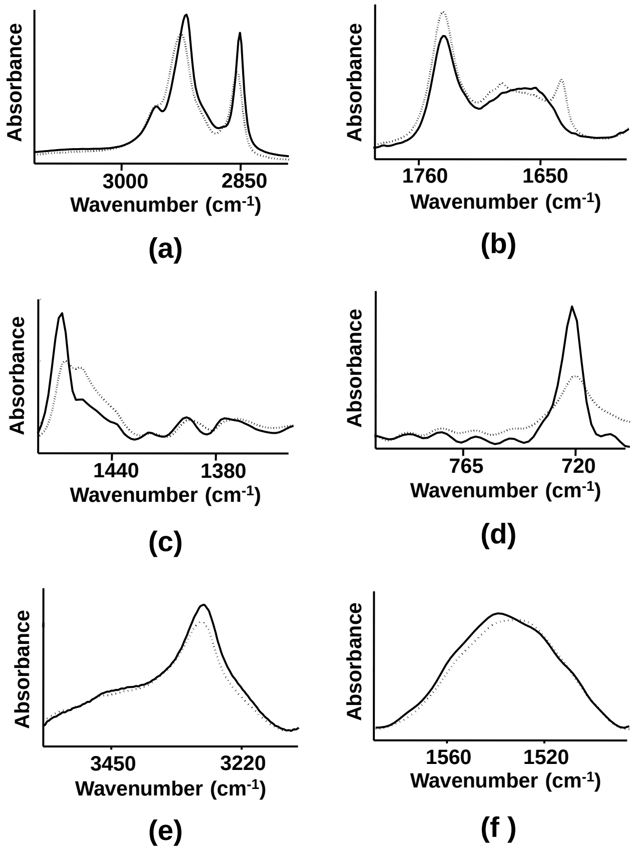

Fig. 5. FT-IR spectra of PSLG corresponding to: (a) CH_2 stretching mode; (b) amide I mode; (c) CH_2 deformation mode; (d) CH_2 rock mode; (e) N–H stretching mode; (f) amide II mode. (solid line: 26°C, dot line: 80°C).

be a mixed mode containing a major contribution from the N–H in-plane deformation [30]. In the case of amide II band, the force field of N–H deformation mode may be considered to be weakened as the strength of N–H···O=C hydrogen bond in the backbone is weakened after the phase transition. Accordingly, the amide II band shifts to lower frequency.

4. Conclusion

In the present study, the infrared spectra of PMLG, PHLG and PSLG have been measured and analyzed in order to understand the side chain effect on the conformation of the α-helical backbone. Both N–H stretching and amide I vibrational bands appear to be shifted to higher frequencies by increasing the side chain length. The results indicate that weaker hydrogen bonds are formed by increasing the length of the side chain. That is, the rigid rod-like property of the α-helical backbone is weakened by increasing the side chain length. The vibrational frequencies calculated at the B3LYP/6-31G(d)//AM1 level for the three polymers strongly support the spectroscopic data with remarkable accuracy.

The variable temperature infrared measurements for PHLG and PSLG have also been performed to examine the effect of temperature on the conformational behavior of the side chains. No frequency shift or intensity change was found in PHLG, and hence no perceptible conformational change has been found by increasing the temperature. However, the intensity changes and frequency shifts of the characteristic vibrational bands have been found for the infrared spectra of PSLG with longer alkyl side chains after the phase transition. The relative broadness of characteristic CH_2 bands over 60°C suggests that the mobility of the long alkyl side chains is increased when the phase is moved from the crystalline to the amorphous state. This increased mobility of the long side chains induces the splitting of the amide I band over the transition temperature. This also takes an effect on the N–H···O=C hydrogen bonding strength in the α-helical backbone. Spectral observations in the N–H stretching and amide II regions are consistent with a reduction of the hydrogen bonding strength after the phase transition.

Acknowledgements

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