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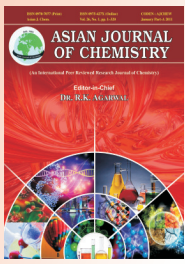

Effect of Sm^{3+} on the Spectroscopic Properties of Poly(N-vinylisobutyramide)

ZHIDU CHEN, SHOUFU YU and SHAOFEN GUO*

Shandong Provincial Key Laboratory of Water and Soil Conservation & Environmental Protection, Linyi University, Linyi 276005, P.R. China

*Corresponding author: Tel/Fax: +86 539 8766700; E-mail: guoshaofen@lyu.edu.cn

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In this paper, the effect of Sm^{3+} on the spectroscopic properties of poly(N-vinylisobutyramide) (PNVIBA) polymer was investigated by using ultraviolet-visible, FT-IR and fluorescent spectroscopy techniques. It was found that Sm^{3+} might coordinate with N atoms in the PNVIBA side chain and form the Sm^{3+}-PNVIBA complex. After forming the Sm^{3+}-PNVIBA complex, the fluorescence emission intensity at 315 nm was significantly enhanced 1.73 times comparing with that of the PNVIBA polymer, in which the efficient intramolecular energy transfer from Sm^{3+} to PNVIBA might be occurred. The Sm^{3+}-PNVIBA complex could transform the short ultraviolet radiation to longer wavelength UV-B band radiation. However, the low critical solution temperature (LCST) of PNVIBA was not obviously changed after the addition of a small amount of Sm^{3+}. This thermosensitive complex might be a potential functional material in many fields.

Keywords: Sm^{3+}, Poly(N-vinylisobutyramide), Fluorescence property, Low critical solution temperature.

INTRODUCTION

Poly(N-vinylisobutyramide) (PNVIBA) was firstly synthesized by Akashi from poly(N-vinylacetamide)[1]. It is one of the thermoresponsive synthetic polymers[1,2] that carry both hydrogen-bonding and hydrophobic properties, which causes changes in their molecular level states in an aqueous solution[3]. The structure of PNVIBA is similar to the structure of poly(N-isopropylacrylamide) (PNIPAAm), but the function groups of C=O and N-H in the side chain are exchanged between the two polymers. As known that PNIPAAm has the low critical solution temperature (LCST) at about 31 ºC[4], the PNVIBA has the LCST near 39 ºC[5]. The experiment showed that PNVIBA is almost nontoxic, meanwhile, its LCST is slightly higher than that of human body temperature and much higher than the LCST of PNIPAAm, thus PNVIBA may be widely used in the field of biological engineering.

In the last few decades, water-soluble monomers and polymers have acquired great importance as biomedical materials in pharmaceutical fields and analytical chemistry. Specially, an interest in the rare earth elements-doped polyamide has been greatly stimulated by their potential applications, such as Tb(III)-PNIPAAm complex[6], Tb(III)-PNIPAAm-*g*-poly(NIPAAm-co-styrene) complex[7], Eu(III)-poly(N-vinylacetamide)[8] and Tb(III)-poly(N-vinylacetamide) complex[9], the complexes display good optical and water-soluble properties. However, the effect of rare earth element on PNVIBA spectroscopic properties has been not reported. In this paper, the effect of Sm^{3+} on PNVIBA spectroscopic properties were investigated with the ultraviolet-visible, FT-IR and fluorescent spectroscopy. It is hoped that the experimental results could provide a reference point on better understanding the application of the thermosensitive polyamide

EXPERIMENTAL

Poly(N-vinylisobutyramide) was provided by Professor Chen and was used without purification. The average molecular weight (Mn) was evaluated with Gel Permeation Chromatographic measurement. The value measured was 66000 g/mol. Samarium (III) chloride ($SmCl_3 \cdot 6H_2O$) was purchased from Aldrich Chemical Co., Inc. All other reagents were of analytical grade.

Preparation of Sm^{3+}-PNVIBA complex: According to the weight ratio of Sm^{3+}:PNVIBA = 0.1 %, 0.2 %, 0.4 %, $SmCl_3$ and PNVIBA were dissolved in ethanol. The mixture solution was stirred and refluxed for 24 h. The product was purified and then dried in a vacuum at the room temperature for 48 h, thus the Sm^{3+}-PNVIBA complex was obtained.

Characterization of Sm^{3+}-PNVIBA complex: UV-visible absorption spectra were obtained using a Shimadzu UV265 (Shimadzu, Japan) recording spectrophotometer with 0.5 cm path length cell. The ethanolic solutions of PNVIBA without and with Sm^{3+} were determined and the ethanol was used as a reference.

The changes in FT-IR spectra for the solutions of PNVIBA with and without Sm^{3+} were determined by a Nexus 670 FT-IR spectrometer (Nicolet, USA). The ethanol solution of PNVIBA without and with Sm^{3+} were cast on TlIBr disks and dried in vacumm respectively and then the samples FT-IR spectra were determined.

A German Perkin-Elmer model Ls50B fluorescence spectrophotometer was used to measure fluorescence spectra of PNVIBA without and with Sm^{3+}. When the relationship between the temperature and the excitation intensity of a fluorescence peak of PNVIBA and the Sm^{3+}-PNVIBA complex was measured, the samples were heated with a slow rate and the excitation spectra were recorded with an interval of 0.5 °C.

RESULTS AND DISCUSSION

UV-visible absorption spectra: Fig. 1 showed the UV-visible spectra of PNVIBA without (a) and with Sm^{3+} (0.1 % wt) (b). In curve a, the peak near 214 nm is due to π-π^* transition of C=O group in the side chain of PNVIBA. Comparing the curve a with curve b, it could be seen that the π-π^* transition peak of amide in Sm^{3+}-PNVIBA complex is broader and the intensity is increased than that of in PNVIBA. In addition, the shoulder peak around 250 nm is appeared in Sm^{3+}-PNVIBA complex, which is corresponding to n-π^* transition of C=O. The results indicated that Sm^{3+} ion may interact with PNVIBA and leading to the energy level reconstruction, so that the n-π^* forbidden transition of C=O was achieved[10]. The interaction between Sm^{3+} ion and PNVIBA resulted in the increase of PNVIBA planarity or the degree of conjugation, thus the absorption intensity was increased.

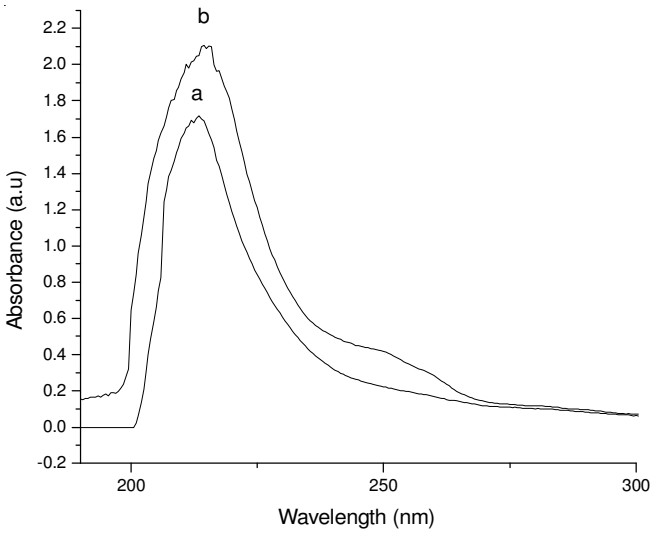

Fig. 1. UV-visible spectra of PNVIBA without (a) and with Sm^{3+} (0.1 % wt) (b)

FT-IR spectra: Fig. 2 showed FT-IR spectra of PNVIBA without (a) and with Sm^{3+} (0.1 % wt) (b). It could be observed from Fig. 2 curve a that there are several absorption bands in the range of bonded vibrations in the following regions: 3400-3200 cm^{-1} for N-H stretching vibration, the bands at 2970 and 2875 cm^{-1} are assigned to the asymmetric and symmetric ν(C-H) vibration of the methyl groups, respectively. The band at 2936 cm^{-1} is ascribed to the asymmetric ν(C-H) vibration of the methylene groups of polymer backbone. The band at 1646 cm^{-1} is ascribed to amide I ν(C=O) and the band at 1546 cm^{-1} is ascribed to amide II (mainly the N-H bending vibration, δ(N-H) (Fig. 2, curve a). In the Sm^{3+}-PNVIBA complex (Fig. 2, curve b), the band of amide I was blue shifted from 1646 cm^{-1} to 1651 cm^{-1} and amide II was slightly red shifted from 1546 cm^{-1} to 1544 cm^{-1}, respectively. Thus, it could be deduced that after Sm^{3+} interacting with N atom in PNVIBA side chain, the part of the lone electron pair of N atoms transfers to the empty orbit in the outer layer of Sm^{3+}. The decrease of N-H and C-N bonds electron density led to the characteristic band of amide II red shift. In addition, the inducement effect led to the electron density increase of C=O double bond and thus the characteristic band of amide I was blue shifted[11]. There is a steric hindrance of isopropyl group near C=O side, which blocked Sm^{3+} to coordinate with O atom in C=O group but coordinated with N atoms.

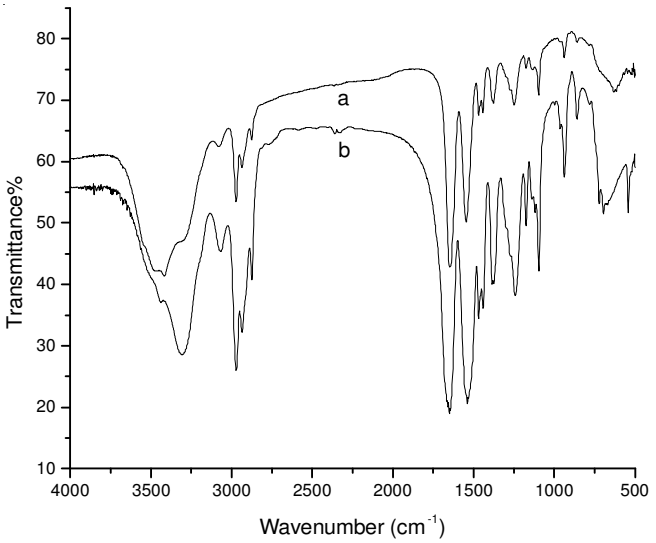

Fig. 2. FT-IR spectra of PNVIBA without (a) and with Sm^{3+} (0.1 % wt) (b) in the 4000-500 cm^{-1} area

Fluorescence spectra: Fig. 3a showed the excitation fluorescence spectra of PNVIBA without (a) and with Sm^{3+} (0.1 % wt) (b). In the excitation fluorescence spectrum of PNVIBA (curve a), a broad excitation peak around 310 nm attributed to the $\pi \rightarrow \pi^*$ transition of C=O group in PNVIBA was observed[6]. Meanwhile, a broad band around 653 nm was appeared. However, in the Sm^{3+}-PNVIBA complex, a sharp peak at 272 nm was observed, the peak shape became sharper than that of in PNVIBA and the intensity was increased 2.5 times, in addition, the broad band around 653 nm was shifted to 574 nm and the intensity was decreased. The above results indicated that Sm^{3+} could interact with PNVIBA and form Sm^{3+}-PNVIBA complex, the complex may have a rigid planar conjugated structure, then affected the conformation and the conjugate area of PNVIBA, resulting in the change of PNVIBA absorption properties[12].

Fig. 3b showed the fluorescence emission spectra of PNVIBA without (a) and with Sm^{3+} (0.1 % wt) (b) under the excitation wavelength at 272 nm. In the fluorescence emission spectrum of PNVIBA, a peak of PNVIBA was located at 315 nm and a weak broad band around at 610 nm. In the

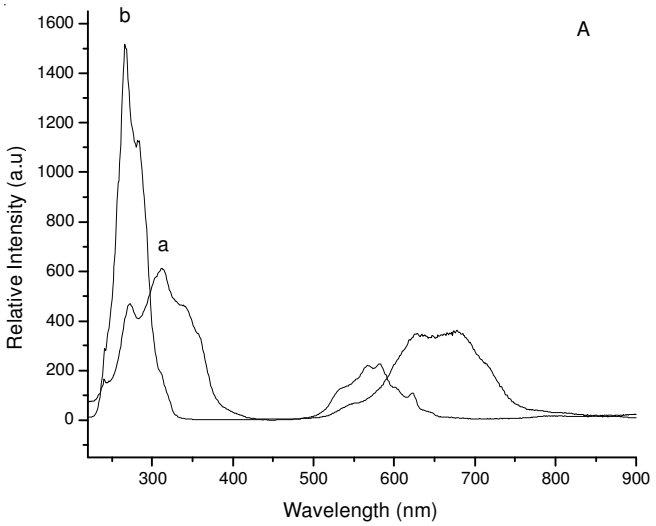

Fig. 3(a). Fluorescence excitation spectra of PNVIBA without (a) and with Sm^{3+} (0.1 % wt) (b). (Excitation slit ex/em = 5/5 nm, Emission wavelength: 400 nm)

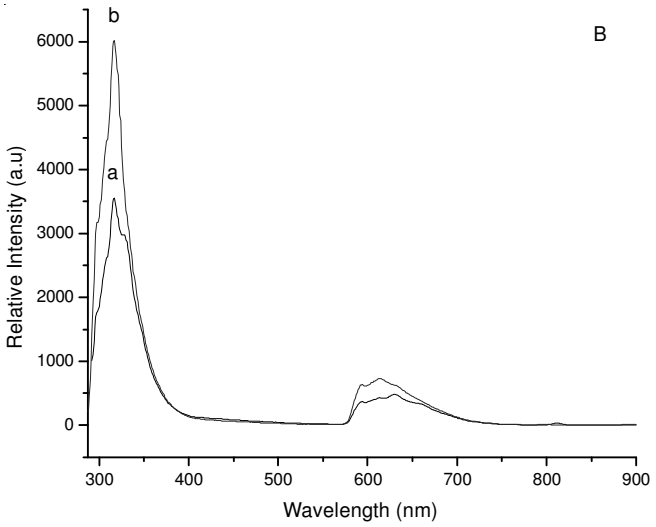

Fig. 3(b). Fluorescence emission spectra of PNVIBA without (a) and with Sm^{3+} (0.1 % wt) (b). (Emission slit ex/em = 3/5 nm, Excitation wavelength: 272 nm)

fluorescence emission spectrum of Sm^{3+}-PNVIBA complex, two broad peaks were located at 315 nm and 610 nm, which according to the PNVIBA fluorescence emission band, but the Sm^{3+} character emission peaks were not observed in 300-600 nm. In addition, the fluorescence intensity at 315 nm and 610 nm were both increased, especially the peak at 315 nm was increased 1.73 times. The results indicated that there was no efficient energy transfer from PNVIBA polymer ligand to Sm^{3+}. One reason should be that the excited triplet state of PNVIBA polymer was not match with 4G5/2 energy level of Sm^{3+}, the polymer absorbed energy can not transfer to Sm^{3+} efficiently. Another possible reason might be that the energy obtained by Sm^{3+} may transfer to PNVIBA through a metal-to-ligand intramolecular charge transfer process as investigated in the composite systems studied earlier[13]. In the Sm^{3+}-PNVIBA complex, the direct coordination of polymer ligand to Sm^{3+} could improve the energy-transfer rates with reducing the distance between the ligand and Sm^{3+}, the energy transfer from Sm^{3+} to PNVIBA was occurred, thus fluorescence intensity of PNVIBA was enhanced.

Low critical solution temperature behavior of Sm^{3+}-PNVIBA: In the experiment, LCST of the Sm^{3+}-PNVIBA complex in the aqueous solution can be measured using fluorescence spectroscopic technique. Fig. 4 showed the relationship between the temperature and the fluorescence excitation intensity of the peak at 272 nm of the Sm^{3+}-PNVIBA complex with the different weight ratios of Sm^{3+}. It could be seen that when the temperature is lower than about 39 °C, the fluorescence excitation intensities changed a little bit with increasing the temperature for all the Sm^{3+}-PNVIBA complexes. When the temperature was higher than 39 ºC, the excitation intensities increased significantly with increasing the temperature, because the conformation of the Sm^{3+}-PNVIBA complex was changed from the hydrophilic coils to the hydrophobic globules and then, the water-soluble Sm^{3+}-PNVIBA complex became to be water-insoluble. Therefore, the temperature at the turning point of the excitation intensity could be considered as LCST of the Sm^{3+}-PNVIBA complexes. It could be observed from Fig. 4 that LCST of PNVIBA was about 39 °C, while LCST of the Sm^{3+}-PNVIBA complexes were almost at 39 °C. The results indicated that a small amount of Sm^{3+} had no obvious effect on the LCST of PNVIBA, but could enhance the polymer's fluorescence emission intensity significantly.

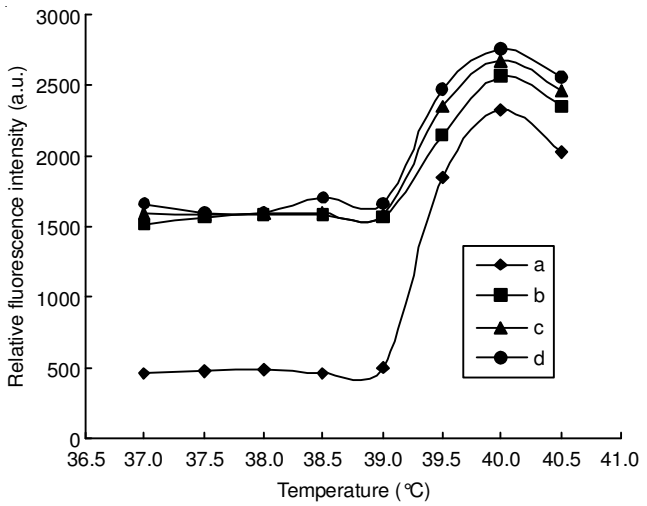

Fig. 4. Relationship between the temperature and the excitation fluorescence intensity of the peak at 272 nm of PNVIBA with the different weight ratios of Sm^{3+}. 0 (a), 0.1 % (b), 0.2 % (c), 0.4 % (d)

Conclusion

From the above experimental results, it could be concluded that when Sm^{3+} interacted with PNVIBA, Sm^{3+} mainly bonded to N of PNVIBA side chain and formed the Sm^{3+}-PNVIBA complex. After forming the Sm^{3+}-PNVIBA complex, the emission fluorescence intensity of Sm^{3+}-PNVIBA complex was significantly enhanced. Especially, the emission intensity of the fluorescence peak at 315 nm was increased as high as 1.73 times comparing with the PNVIBA. Small amount of Sm^{3+} had no obvious effect on the LCST of PNVIBA, but could enhance the polymer's fluorescence emission intensity significantly. The Sm^{3+}-PNVIBA complex could absorb the

short ultraviolet radiation then transform to longer wavelength UV-B radiation and the complex might be a potential biomedical material.

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