

## Synthesis and Characterization of Samarium (III) Containing Poly-(N-vinylacetamide) Complex

Yan CAI<sup>1</sup>, Ming Qing CHEN<sup>1</sup>, Juan XU<sup>2</sup>, Pin Fang WU<sup>1</sup>, Akashi MITSURU<sup>1,3</sup>,  
Xiao Hua HUANG<sup>1,2\*</sup>

<sup>1</sup>School of Chemistry and Material Engineering, Southern Yangtze University, Wuxi 214036

<sup>2</sup>College of Chemistry and Environment Science, Nanjing Normal University, Nanjing 210976

<sup>3</sup>Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering,  
Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

**Abstract:** Poly (N-vinylacetamide) (PNVA) was synthesized by the free radical polymerization and its samarium (III) binary complex was prepared and characterized by means of IR, UV-vis, X-ray photoelectron spectroscopy (XPS) and fluorescence spectra. The fluorescent intensity of samarium (III) characteristic emission was increased significantly due to efficient energy transfer from polymeric ligand to Sm (III) ion in the complex.

**Keywords:** Samarium, poly (N-vinylacetamide), complex, fluorescence.

In recent years, interest in rare earth doped polymers has been greatly stimulated by their potential use in fluorescence and laser systems<sup>1</sup>. Poly (N-vinylacetamide) (PNVA) is considered as promising polymer for medical and biological function material not only for its avirulence and solubility in water and organic solvents, but also as a precursor to poly (vinylamine)<sup>2</sup>. In this paper, we developed Sm(III) containing PNVA as a novel potential medical and biological luminescent material. PNVA was synthesized by free radical polymerization in the presence of AIBN as initiator at 60 °C for 8 h. Then, ethanol solution of SmCl<sub>3</sub> and PNVA was mixed and stirred at 55 °C for 24 h. Subsequently, the PNVA and Sm(III) containing PNVA (Sm(III)-PNVA) were characterized by IR, UV, XPS and fluorescence spectra.

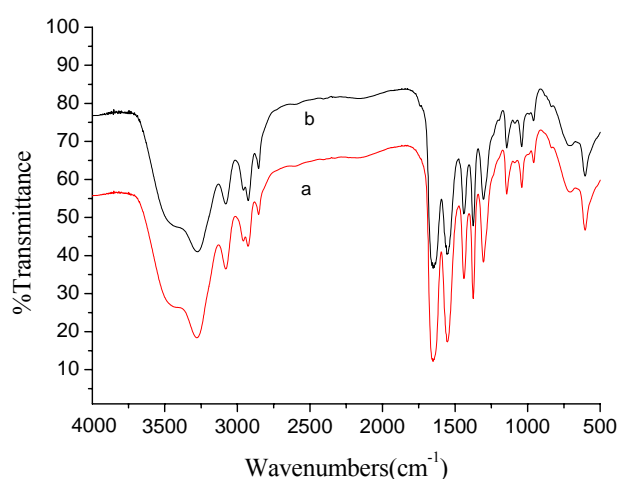
Infrared spectra of the PNVA (a) and Sm(III)-PNVA (b) are shown in **Figure 1** (TJ270-30 infrared spectrophotometer, Tianjin Optical Apparatus Corporation). Sm(III)-PNVA and free polymer ligand showed similar shape of IR spectrum, but their absorption bands of coordination groups displayed differential wave numbers. The vibrational absorption band of C=O in the Sm(III)-PNVA was shifted to a lower frequency (from 1649 to 1644 cm<sup>-1</sup>) and the composite absorption band of  $\delta_{\text{NH}}$  and  $\nu_{\text{CN}}$  was shifted to a higher frequency (from 1551 to 1556 cm<sup>-1</sup>), indicating that Sm(III) ion possibly bonded to oxygen atom of carbonyl group in PNVA<sup>3,4</sup>.

---

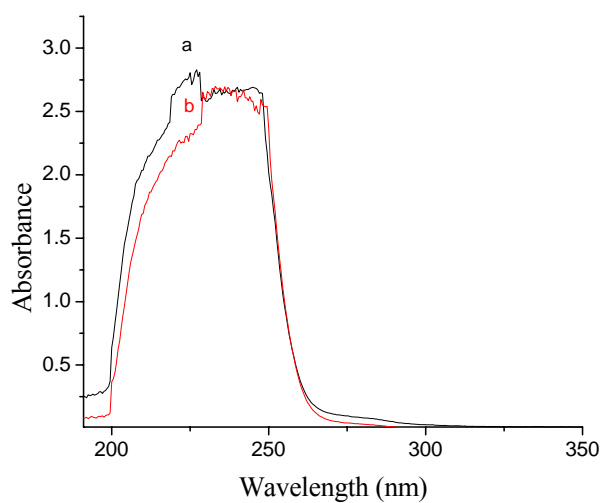
\*E-mail: wxhhuang@yahoo.com

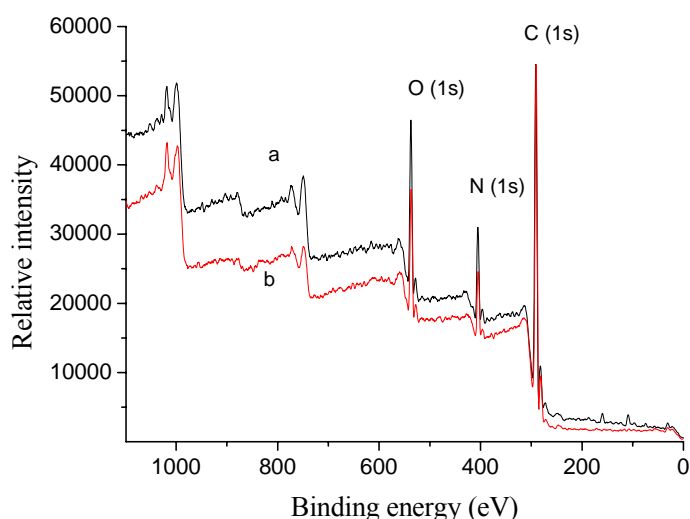
The UV-Vis spectra were recorded by a UV1100 spectrophotometer (Beijing Ruili Analytical Apparatus Corporation). **Figure 2** showed the absorption spectra of PNVA (a) and Sm(III)-PNVA (b) in range from 190 to 400 nm. Compared with PNVA, the maximum absorption peak of Sm(III)-PNVA, which corresponding to  $\pi \rightarrow \pi^*$  transition of carbonyl group, is red shifted from 245 to 250 nm. The phenomenon indicated that Sm(III) ion probably bonded with oxygen atom and the difference of energy of  $\pi \rightarrow \pi^*$  transition reduced<sup>4</sup>.

**Figure 1** IR spectra of PNVA (a) and Sm(III) containing PNVA (b)



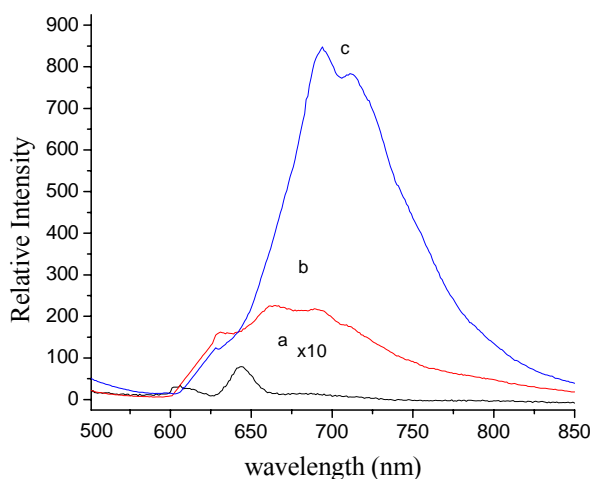
**Figure 2** UV spectra of PNVA (a) and Sm(III) containing PNVA (b)



**Figure 3** XPS spectra of PNVA (a) and Sm(III) containing PNVA (b)

The XPS spectra were recorded (ESCALAB 2201-XL XPS spectrometer) with  $AlK\alpha$  (1486.6 eV) as the excitation source on the analyzed area of the polymer material. The X-ray source power is  $15\text{ kV} \times 20\text{ mA}$ . The analysis was performed under a residual pressure less than  $5 \times 10^{-7}$  Pa. Firstly, the change of binding energy indicated that the moving state of density of core-level electrons was affected by binding with Sm(III) ion, or forming the complex of Sm(III)-PNVA<sup>5</sup>. Secondly, the binding energy peak near 533 eV, corresponding to average binding energy of O (1s) of C=O bonds, was shifted from 532.64 to 533.35 eV after adding Sm(III) ion. Meanwhile, the N (1s) binding energy of C-N bond around 401 eV was shifted from 401.13 to 401.53 eV. The results demonstrated that the electron density of O and N atoms in PNVA was decreased, respectively<sup>6</sup>. Therefore, Sm(III) ion could bind to O atom of carbonyl group or N atom of amido group and formed the Sm(III)-PNVA complex.

The fluorescence emission spectra of Sm(III) ion (a), PNVA (b) and Sm(III)-PNVA (c) are shown in **Figure 4**. The weak emission peak at 680 nm is corresponding to  ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$  transition of Sm(III) ion (**Figure 4**, curve a). PNVA shows a broad emission band from 600 nm to 800 nm (**Figure 4**, curve b). The emission peaks of Sm(III)-PNVA complex shows a peak at 694 nm (**Figure 4**, curve c), which belongs to the  ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$  transition of Sm(III) ion, increased about 7644% of intensity compared with the emission intensity of Sm(III) ion. The intensity of the shoulder peak near 712 nm that assigned to the  ${}^4G_{5/2} \rightarrow {}^6H_{11/2}$  transition is approximately 11298% stronger than that of  $SmCl_3$ . As we know, rare earth ions are incorporated in organic chelates by coordination through a donor atom such as oxygen; when the ligand was excited by UV light, they exhibit narrow-line emission at approximately the same frequencies as the inorganic crystal system. This phenomenon is the result of an intermolecular energy transfer from the electronic states associated with the organic complex to localized intra-4f shell energy levels of the ions<sup>7</sup>.

**Figure 4** Emission spectra of Sm(III) (a), PNVA (b) and Sm(III)-PNVA complex (c)

Excitation wavelength = 308 nm, Slit ex / em = 5/5 nm

Obviously, it is the reason that the formation of Sm(III)-PNVA complexes enhanced the fluorescence intensity of the rare earth ion  $\text{Sm}^{3+}$ .

### Acknowledgments

This project is supported by the National Natural Science Foundation of China (No.20243002), National Planning Commission Foundation of China (No.GJX01100626), the Foundation of Science and Technology Committee of Jiangsu Province (No.BG2001045) and the Natural Science Foundation of Education Committee of Jiangsu Province (01KJB150006).

### References

1. M. Nishiya, S. Sasaki, H. Taniguchi, J. Kido. *Appl. Phys. Lett.*, **1995**, 67, 1060.
2. M. Akashi, E. Yashima, T. Yamashita, N. Miyauchi, *J. Polym. Sci.: Part A: Polym. Chem.*, **1990**, 28, 3487.
3. Y. P. Wang, Z. Q. Lei, H. Y. Feng, *et al.*, *J. Applied. Polym. Sci.*, **1992**, 45, 1641.
4. H. Y. Feng, S. H. Jian, Y. P. Wang, *et al.*, *J. Applied. Polym. Sci.*, **1998**, 68, 1605.
5. D. P. Drolet, A. J. Lees, *Inorganica Chimica Acta*, **1988**, 150, 197.
6. M. Wirde, U. Gelius, L. Nyholm, *Langmuir.*, **1999**, 15(19), 6370.
7. H. F. Brito, O. L. Malta, M. C. F. C. Felinto, *et al.*, *J. Alloys and Compounds*, **2002**, 344, 293.

Received 18 August, 2003