Fluorescence properties of the terbium salt of sulfonated poly(ether ether ketone)

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Poly(ether ether ketone) (PEEK) was used to prepare a sulfonated terbium salt (Tb-SPEEK). This salt emits green fluorescent light under u.v. excitation. The fluorescence originates from the transition of the $^5D_4$ level of Tb^{3+} to the levels of ^7F_J ($J=6, 5, 4, 3$). The fluorescence intensity increases with increasing Tb content, reaching a maximum value at around 9 wt% Tb, and then decreases due to the formation of ionic aggregates in the salt. The excitation of the salt is related to its Tb content and corresponding solid state, and changes after experiencing thermal treatment.

(Keywords: poly(ether ether ketone); terbium salt; fluorescence)

Introduction

Poly(ether ether ketone) (PEEK) has increasingly found applications in high-performance composites, wires and cables for nuclear plants and oil wells because of its excellently balanced properties[1,2]. It has been reported that PEEK is soluble only in a few solvents, such as 98% sulfuric acid and hydrofluoric acid, at room temperature. When dissolved in concentrated sulfuric acid, or its mixture with methanesulfonic acid, PEEK becomes sulfonated[3–5]. The reaction not only modifies the solution behaviour of PEEK in the acids, but also changes its solid morphology, thermal properties and makes it soluble in some common solvents. An amorphous polymer with high glass transition temperature (T_g), lower thermal stability and good solubility will be obtained when the degree of sulfonation reaches a certain value. The neutralization of such a sulfonated PEEK will cause its T_g to increase greatly and its thermal stability to improve.

When the compound of a rare earth ion (terbium) was used to neutralize the sulfonated PEEK, the obtained polymeric salt was found to be strongly fluorescent under u.v. light excitation[6]. Its T_g is around 200°C but the onset decomposition temperature exceeds 390°C. The balanced fluorescence and thermal properties of such modified PEEK are much better than those of the other polymeric–rare earth ion complexes reported previously, and could make it more applicable in areas such as laser systems. In this paper, the fluorescence of the terbium salt of sulfonated PEEK is studied.

Experimental

PEEK powder, with a reduced viscosity of 0.68 ml g^{-1} was provided by Professor Zhongwen Wu at Jilin University, P.R. China. It was dissolved in concentrated H_2SO_4 and stirred at room temperature for the desired time, then precipitated with additional distilled water and washed to completely remove excess acid. After drying, the obtained sulfonated PEEK was dissolved in alcohol, then the excess alcohol solution of $TbCl_3$ was added into it at a certain temperature[6]. The resulting salt (Tb-SPEEK) was collected, dried in vacuum at 90°C for 24 h and ground before measurement.

The sulfonation degree of the sulfonated PEEK was determined by titrating with NaOH in aqueous solution and was expressed as mole per cent, the number fraction per repeat unit considering each phenyl ring as capable of being sulfonated[4]. Meanwhile, the Tb content in the salt was determined by an ash method, as follows. A weighed sample in a porcelain crucible was placed in a furnace, heated to 700°C and held for 4 h. It was then cooled naturally; the obtained ash was dissolved in HCl to get a final aqueous solution, then titrated with an ethylene diamine tetraacetic acid solution of 0.00507 N.

A Hitachi-850 fluorescence spectrophotometer was used to measure the fluorescence spectra of the Tb-SPEEK. The powder sample was placed in the solid sample holder attached to the instrument, and the measurement was carried out at room temperature.

Results and discussion

The Tb-SPEEK emits green fluorescent light under u.v. light excitation. *Figures 1* and *2* show its typical excitation spectrum and emission spectrum, respectively. Two excitation peaks at 258 and 358 nm are seen. Such excitation is different from that of Tb salts of the various copolymers of acrylic acid[7] and Tb salt of sulfonated polystyrene[8], indicating a distinctive mechanism in Tb-SPEEK. By comparing with the typical features of a Tb^{3+} complex in solution[9], and calculating the energy difference between the various levels of Tb^{3+}, the bright-green fluorescence emission lines of the salt are assigned to transitions from the $^5D_4$ level of Tb^{3+} to the levels of $^7F_6$, $^7F_5$, $^7F_4$, $^7F_3$, as illustrated in *Table 1*. The intensity of the $^5D_4 \rightarrow {}^7F_5$ is the strongest emission, in agreement with the reported fluorescent transition characteristics of such ions[9].

The dependence of the fluorescence intensity, at 545 nm under excitation of 358 nm, on Tb content in the salt is shown in *Figure 3*. The intensity increases greatly with increasing Tb content and reaches a maximum at around 9 wt%, then decreases with further increase of the ion. A similar relationship between fluorescence intensity and ion content was found in some polymer–europium com-

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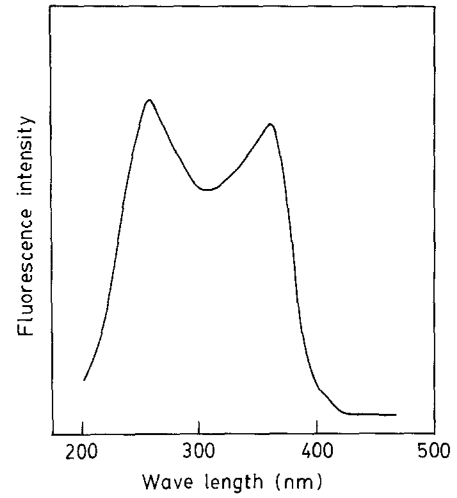

Figure 1 Excitation spectrum of Tb salt of sulfonated PEEK. Tb content 9.8 wt%, sulfonation degree, X_s, in the salt 32 mol%, $\lambda_{Em}=545$ nm

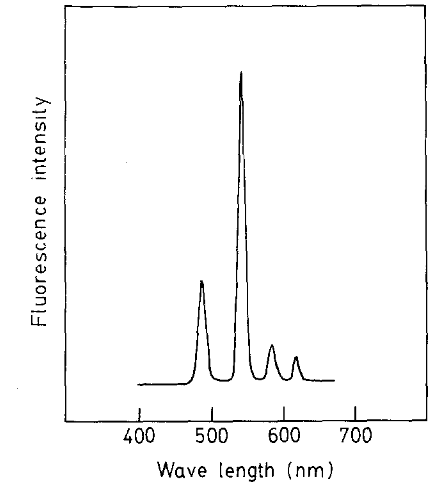

Figure 2 Emission spectrum of Tb salt of sulfonated PEEK. Tb content 9.8 wt%, sulfonation degree, X_s, in the salt 32 mol%, $\lambda_{Ex}=358$ nm

Table 1 Fluorescence emission lines of Tb-SPEEK

Wavelength (nm)[a]	Peak intensity[b]	Transition
490	32.5	$^5D_4 \rightarrow {}^7F_6$
545	100	$^5D_4 \rightarrow {}^7F_5$
590	9	$^5D_4 \rightarrow {}^7F_4$
625	3.9	$^5D_4 \rightarrow {}^7F_3$

[a] Excitation at $\lambda_{Ex}=358$ nm
[b] Normalized to the most intense emission $^5D_4 \rightarrow {}^7F_5$

plexes containing various acrylic acids; the formation of ionic aggregates in which the ions are close together was thought to be the reason for the intensity depression[7,10]. Bailly *et al.*[5] found that ionic clusters form in the sodium salt of sulfonated PEEK when the sodium sulfonate concentration reaches a critical value of 10–30 mol%. It is responsible for the change in slope in the T_g *versus* ion content curve and the broadening of the glass transition, reflecting structural fluctuations in the salt. In Tb-SPEEK the half-width of T_g (ΔT_g) was determined to be 5°C at 6.1 wt% Tb, but 12°C at 11 wt% Tb. Therefore, a significant amount of ionic aggregate or cluster is present in Tb-SPEEK when the Tb content is higher.

The Tb content in the salt is a function of the sulfonation degree of PEEK, X_s, as shown in *Figure 4*. Although excess Tb^{3+} was used in the reaction, the increase of Tb content with X_s becomes less after X_s reaches nearly 30 mol%. The reason is that the formation of ionic aggregate constrains the molecular chains, therefore reducing the possibility of reaction of the unreacted sulfonic acid groups in the chains. Due to the dependence of Tb content on X_s in the salt, X_s is suggested to have an effect on the depression in the fluorescence intensity. It was found that the salt gradually changed from white to brown with a further rise in X_s after it reached 30–40 mol%. Since light absorption is usually stronger in a dark-coloured sample, the re-absorption of the Tb^{3+} emission by the salt is more likely when the sample is brown, corresponding to higher Tb content and higher value of X_s, and therefore might affect the detected fluorescence intensity[10]. For this reason, X_s should be considered together with Tb content.

Another influence of the ion content on the fluorescence

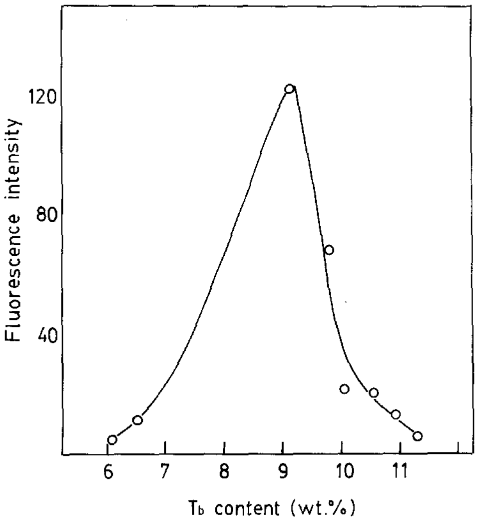

Figure 3 Relationship between fluorescence intensity at $\lambda_{Em}=545$ nm and Tb content. $\lambda_{Ex}=358$ nm

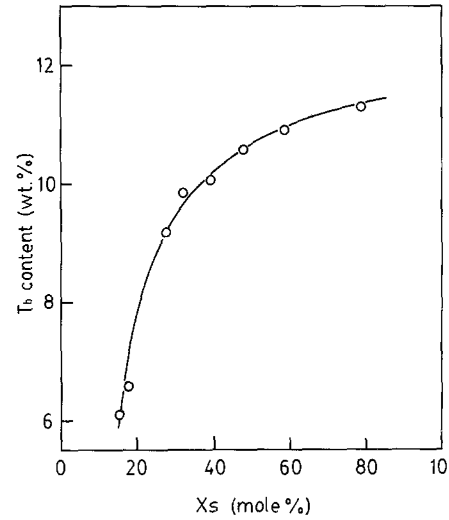

Figure 4 Tb content in the salt as a function of sulfonation degree, X_s

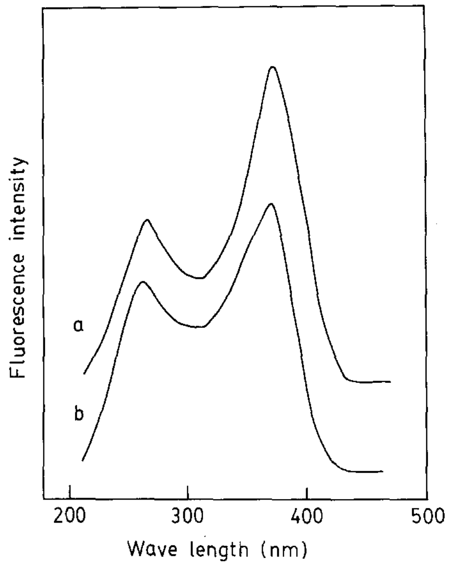

Figure 5 Excitation spectrum of Tb salt of sulfonated PEEK: a, Tb content 6.1 wt%, sulfonation degree, X_s, in the salt 15.6 mol%; b, Tb content 9.8 wt%, sulfonation degree, X_s, in the salt 32 mol%. The salt was treated at 250°C for 5 h. $\lambda_{Em} = 545$ nm

of Tb-SPEEK was observed in the excitation process. As seen in *Figure 5a*, the intensity of the low-wavelength excitation peak is lower than that of the high-wavelength peak when Tb content is lower, related to a lower sulfonation degree, X_s. This characteristic is distinctly different from that in *Figure 1*, which is similar to the excitation spectra of the salts with Tb content over 9.8 wt%, and associated value of X_s over 32 mol%. The difference means that the ratio of the number of emitted photons at lower wavelength of excitation light to that at higher wavelength depends on the Tb content in the salt. However, when the sample with a higher intensity peak at lower wavelength is thermally treated, its excitation spectrum may change into that with a higher peak at higher wavelength. *Figure 5b* shows a varied excitation spectrum obtained when the same salt as in *Figure 1* was held at 350°C for 5 h. Since Tb-SPEEK begins to degrade at 390°C, treatment at 350°C should not result in variation in its chemical structure, but in its physical one. These phenomena are considered to be related to the solid state of the salts. As discussed above, ionic aggregates form when Tb content is higher. In such salts, it is possible that Tb^{3+} is more difficult to excite and higher excitation energy is needed. So more photons are emitted at low wavelength. When the salts are thermally treated at a temperature much higher than their T_g, their chain mobility might reduce the ionic aggregate, making Tb^{3+} more easily excited under lower excitation energy.

The europium salt of sulfonated PEEK was also prepared and was found to emit red fluorescent light. Sulfonated PEEK can therefore be used as a fluorescent polymeric ligand to rare earth metals. It is characterized by its sulfonated backbone chains differing from the polymers whose side groups are functional, such as sulfonated and carboxylated polystyrene[7]. In neutralization, rare earth ions are directly bonded to the sulfonic acids and might partially coordinate with the carbonyls attached to the backbones. By analysing with Fourier transform i.r., it is found that the absorption of carbonyl at around 1600 cm^{-1} becomes wider, and those at 1414 and 1309 cm^{-1} change to 1408 and 1312 cm^{-1}, respectively, after a sulfonated PEEK is reacted with Tb^{3+}. The coordination between the carbonyl and the ion is thought to be in favour of energy transfer, based on the study of other systems[11,12].

Conclusion

Sulfonated PEEK is a new fluorescent polymeric ligand to rare earth metals. Its terbium salt emits green fluorescent light under u.v. excitation, while its europium salt emits red light. The emission of the Tb salt results from the transition of the $^5D_4$ level of Tb^{3+} to the levels of ^7F_J ($J = 6, 5, 4, 3$). With increasing Tb content in the salt, the fluorescence intensity increases to a maximum value at around 9 wt% Tb and then decreases. The depression in the intensity is due to the formation of ionic aggregates, and might also be related to the sulfonation degree. The ion content will affect the excitation of the salt, and so will thermal treatment at a temperature above 300°C. A possible reason is associated with the ionic aggregate in the salt at high ion content, and its variation after thermal treatment.

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References

1 Searle, O. B. and Rfeiffer, R. H. *Polym. Eng. Sci.* 1985, **25**, 474
2 Wigotsky, V. *Plast. Eng.* 1986, **42**, 17
3 Devaux, J., Delimoy, D., Daoust, D., Legras, R., Mercier, J. P., Strazielle, C. and Nield, E. *Polymer* 1985, **26**, 1994
4 Jin, X. G., Bishop, M. T., Ellis, T. S. and Karasz, F. E. *Br. Polym. J.* 1985, **17**, 4
5 Bailly, C., Williams, D. J., Karasz, F. E. and Macknight, W. J. *Polymer* 1987, **28**, 1009
6 Zhang, Z. Y., Wu, S. L. and Zeng, H. M. Chinese patent CN 91 104 699.2
7 Okamto, Y., Ueba, Y., Dzhanibekov, V. F. and Banks, E. *Macromolecules* 1981, **14**, 17
8 Lu, H., Li, G. F., Fang, S. B. and Jiang, Y. Y. *J. Appl. Sci.* 1990, **39**, 1389
9 Bunzli, J. C. G. and Choppin, G. R. 'Lanthanide Probes in Life, Chemical, and Earth Science', Elsevier, Amsterdam, 1989, p. 218
10 Banks, E., Okamoto, Y. and Ueba, Y. *J. Appl. Polym. Sci.* 1980, **25**, 359
11 Ueba, Y., Zhu, K. J., Banks, E. and Okamoto, Y. *J. Polym. Sci., Polym. Chem. Edn* 1982, **20**, 1271
12 Ueba, Y., Banks, E. and Okamoto, Y. *J. Appl. Polym. Sci.* 1980, **25**, 2007