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Assembly of luminescent hybrids from co-polymers bearing functional 4-vinyl pyridine and europium aromatic carboxylate

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Abstract

Three binary europium complexes with benzoic acid and *ortho* (*meta*) methylbenzoic acids in the first stage. Then, these complexes were introduced into 4-vinyl pyridine-ethyl methacrylate co-polymer hosts using the former component as the second ligand. The composition of the hybrids was characterized by FT-IR and the photophysical property of them was investigated by UV spectra, luminescent spectra and luminescent lifetimes. The experiment results substantiate that 4-vinyl pyridine could co-ordinate to europium ions effectively with nitrogen atoms of the pyridine ring. Therefore, the intramolecular energy transfer process accomplished within polymer hybrids and red emissions of Eu^{3+} have been obtained.

Keywords: Europium ions; 4-Vinyl pyridine-methacrylate co-polymer; Luminescence; Hybrids

1. Introduction

In past decades, relevant research on the lanthanide complexes has grown extensively since Lehn pointed out that such complexes could be used as light conversion molecular devices [1], namely the term “antenna effect” to describe the absorption, energy transfer, emission processes, thus solving the problem of very low absorption coefficients of the lanthanide ions. The design of efficient rare earth complexes has attracted the attention of many research groups, focusing on the diverse classes of ligands, β-diketones [2–4], heterocylic ligands [5,6], cryptands [7], calixarenes [7–9], etc. Zolin et al. have systemically investigated the luminescence and co-ordination structure of ternary lanthanide complexes [10–16]. Our group puts emphasis on the photoactive lanthanide ions (Eu, Tb, Sm, Dy) complexes with aromatic carboxylic acid, bipyridyl or their derivatives [17–22]. As a matter of fact, fluorescent lanthanide complexes may find quite a few practical accounts, such as luminescent probes in biomedical assays, electro-luminescent devices, extraction, separation, germicide preparation, catalysis, etc. [23–26]. In recent years, more attention has been paid to the sol–gel method in the development of luminescent rare earth hybrid materials [27,28]. In addition, the preparation methods have gradually turned into strong covalently bonded composites in contrast to the previous hybrids only through physical mixture [29–37]. Franville et al. have devoted to the modification of pyridine–dicarboxylic acid or their derivatives [33]. Zhang and co-workers dedicated to modification of heterocyclic ligands including 1,10-phenanthroline and di-pyridine [29,30] in order to construct molecular-based hybrids. Our research team at present did considerable work in the preparation of −NHC(=O)NH− urea bridges connecting both siliceous backbone and aminobenzoic acids [31,36,37]. However, several shortcomings still have made them prohibited from practical applications, essentially because rare earth complexes and inorganic backbone are expected to have the desired mechanical flexibility or they have many problems in processing. Furthermore, most lanthanide complexes including their hybrid materials frequently contain too many inner-co-ordinated water molecules, which bring to low emission

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quantum efficiency due to the non-radiative dissipation of energy on the high energy –OH vibrations.

Based on inheriting the merits of both the pure emission color of lanthanide ions and polymer material properties of plastics, polymer-based rare earth luminescent materials have emerged recently [38–43]. Wang et al. [43] have prepared Eu(III)-acrylate-β-diketones monomers and methyl methacrylate co-polymers, indicating that Eu complexes are uniformly bonded to the polymer chain. In this context, we give a simple synthetic approach to construct a series of luminescent Eu-containing polymers. For the sake of restricting steric hindrance effect, we intend to obtain the co-polymers of 4-vinyl pyridine (VP) and ethyl methacrylate (EMA); subsequently, co-ordination behavior occurred among Eu^{3+}, benzoic acid (*ortho* and *meta*) methylbenzoic acids and 4-vinyl pyridine. Furthermore, we selected pyridine instead of Wang's acrylate to see its sensitizing function as a second ligand like 1,10-phenanthroline and bi-pyridine using co-ordinated nitrogen atoms. The luminescence properties of Eu co-polymers were investigated and the energy transfer mechanism completes smoothly through these rare earth polymer systems.

2. Experimental

2.1. Chemicals and procedures

4-Vinyl pyridine was provided by Lancaster Synthesis Ltd. Ethyl methacrylate was the domestic chemical products and used after purification by vacuum distillation. The solvents used were purified by common methods. A typical procedure for the preparation of co-polymers (VP-EMA) was by radical polymerization of 20 ml ethyl methacrylate and 10 ml 4-vinyl pyridine in 20 ml dehydrate tetrahydrofuran (THF) at 65 °C for 10 h, using 125 mg AIBN as initiator. The yield is 82% after purification applying methanol as precipitation reagent. The content of 4-vinyl pyridine unit in co-polymer is 21 mol%, as determined by ^1H NMR spectroscopy. The number average molecular weight and molecular dispersity of co-polymers were 5.7×10^5 and 1.48, respectively, as determined with gel-permeation chromatography (GPC) calibrated by polystyrene standards. The preparation of europium polymers was as follows: 0.25 g co-polymers was dissolved in 5 ml THF with stirring, 1.5 mmol benzoic acid (BA), *ortho* methylbenzoic acid (OMBA) or *meta* methylbenzoic acid (MMBA) was added to the solution then NaOH was used to adjust the pH value of 6–7. A 0.5 mmol $Eu(NO_3)_3 \cdot 6H_2O$ was finally put into the mixture. The mole ratio of 4-vinylpyridine units: $Eu(NO_3)_3 \cdot 6H_2O$: BEN (OBEN, PBEN) was 1:1:3. After stirring for 12 h, the reactive mixture was filtered to give white powders, which were washed five times with THF and dried under vacuum at room temperature (the basic structure of the hybrid polymers $Eu(BA)_3$-VP-EMA was described in Fig. 1). The complexes of europium with the three aromatic carboxylic acids were prepared using chemical co-precipitation and the compositions of them were determined with elemental analysis. Anal. calcd. for $C_{21}H_{23}EuO_{10}$: C, 42.94; H, 3.95; found: C 42.72; H, 3.69. Anal. calcd. for $C_{24}H_{25}EuO_8$: C, 45.58; H, 4.25; found: C 46.02; H, 4.09. For $C_{24}H_{27}EuO_9$: C, 47.15; H, 4.45; found: C 46.92; H, 4.19.

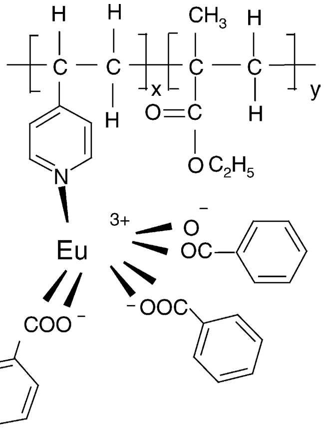

Fig. 1. Scheme for the composition and predict of structure of hybrid polymers $Eu(BA)_3$-VP-EMA, both $Eu(OMBA)_3$-VP-EMA and $Eu(MMBA)_3$-VP-EMA belong to the similar scheme.

2.2. Measurements

All measurements were completed under room temperature. Elemental analysis (C, H, N) was carried out by an Elementar Cario EL elemental analyzer. FT-IR spectra were measured within the 4000–400 cm^{-1} region on an infrared spectrophotometer with the KBr pellet technique. ^1H NMR spectra was recorded in $CDCl_3$ on a Bruker AVANCE-500 spectrometer with tetramethylsilane (TMS) as internal reference. Ultraviolet absorption spectra of these powder samples (5×10^{-4} mol L^{-1} chloroform ($CHCl_3$) solution) were recorded with an Agilent 8453 spectrophotometer. Fluorescent excitation and emission spectrums were obtained on a Perkin-Elmer LS-55 spectrophotometer: excitation slit width = 10 nm, emission slit width = 5 nm. Luminescent lifetimes for hybrid polymer materials and complexes were obtained with an Edinburgh FLS920 phosphorimeter.

3. Results and discussion

No apparent absorption band appear in higher frequency than 2000 cm^{-1} and Fig. 2 shows the FT-IR spectra of (A) co-polymers (VP-EMA) and (B) $Eu(BA)_3$-VP-EMA at the range of 2500–400 cm^{-1}. Both (A and B) have a strong band at around 1722 cm^{-1}, which was ascribed to the absorption of carbonyl groups of EMA. The two peaks at 1599 and 1560 cm^{-1} in (A) correspond to the stretching vibration of C=N in pyridine ring. While in (B), the above two absorptions shifted to 1593 and 1532 cm^{-1} proving that 4-vinyl pyridine units in the co-polymers participated in the co-ordination to

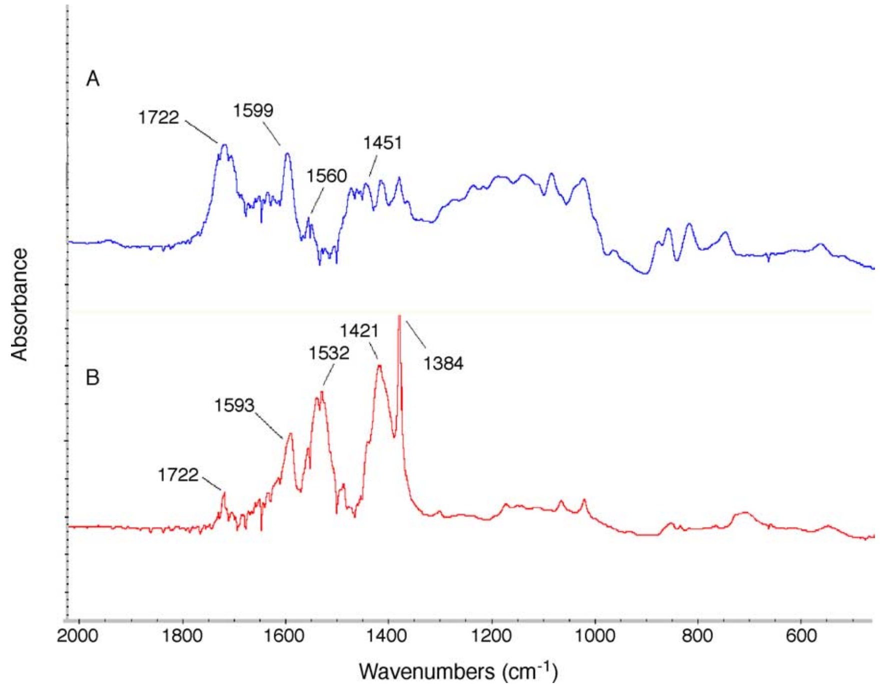

Fig. 2. FT-IR spectra of (A) co-polymers (VP-EMA) and (B) $Eu(BA)_3$-VP-EMA.

europium ions. Likewise, absorptions at 1451 cm^{-1}, which indicated the stretching vibration of C=C groups also red shifted to 1421 cm^{-1} further revealing the occurrence of complexation between Eu^{3+} and pyridine ring. The presence of a new band at 1384 cm^{-1} in (B) belongs to the absorption attributing to symmetrical stretching vibration of carboxylic groups in benzoic acid. Besides, $Eu(OMBA)_3$-VP-EMA and $Eu(MMBA)_3$-VP-EMA exhibit the similar IR spectra.

Fig. 3 exhibits ultraviolet absorption spectra of (A) VP-EMA, (B) $Eu(BA)_3$-VP-EMA, (C) $Eu(OMBA)_3$-VP-EMA and (D) $Eu(MMBA)_3$-VP-EMA. From the spectra, it is observed that the obvious broad band at 255 nm was due to the major π–π* electronic transitions occurred in 4-vinyl pyridine conjugating units. After co-ordinating to europium ions, the absorptions were totally different from co-polymers from two points. On the one hand, the sharp peaks at 247nm come from π–π* electronic transitions of benzoic (*ortho* and *meta* methyl benzoic) acids. Furthermore, the large band at 255 nm contributed by VP-components change into small shoulder peaks located at about 275 nm, again substantiating the complexation of nitrogen atoms and europium ions. This verifies that our basic idea of utilizing 4-vinyl pyridine as sensitizing ligand was partly realized for the three resulting hybrid polymers all exhibit strong characteristic emissions of europium ions as discussed in detail below.

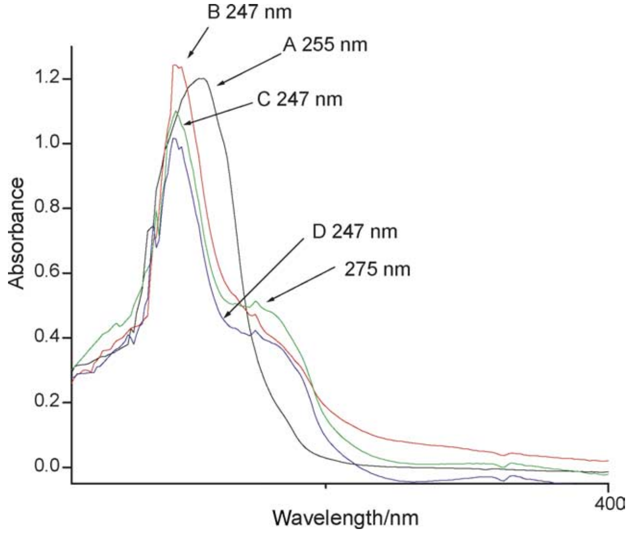

Fig. 3. Ultraviolet absorption spectra of (A) VP-EMA, (B) $Eu(BA)_3$-VP-EMA, (C) $Eu(OMBA)_3$-VP-EMA and (D) $Eu(MMBA)_3$-VP-EMA.

The excitation and emission spectra of the resulting hybrid materials are shown in Figs. 4 and 5. The excitation spectra (Fig. 4) was obtained by monitoring the emission of Eu^{3+} at 614 nm and dominated by a series of broad bands centered at 245 nm and nearby in the ultra-violet region, which is the characteristic absorption of the lanthanide complexes arising from the efficient transition based on the conjugated –C=O double bonds of benzoic acids. As a result, the emission lines of the hybrid material were obtained from the $^5D_0 \rightarrow {}^7F_J$ ($J = 1$–4) transitions for europium ions (Fig. 5A–C) under the excitation wavelength at 245, 245 and 248 nm, respectively, which indicated that the effective energy transfer took place between the $(BA)_3$-VP-EMA ($(OMBA)_3$-VP-EMA or $(MMBA)_3$-VP-EMA) and the chelated RE ions. Among these emission peaks, red emission intensities (arbitrary unit, a.u.) to electric dipole transition of $^5D_0 \rightarrow {}^7F_2$ (43.80 (615 nm)

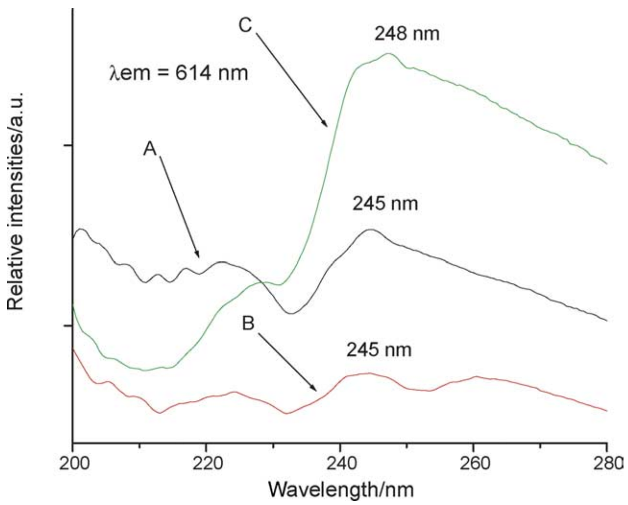

Fig. 4. The excitation spectra of (A) $Eu(BA)_3$-VP-EMA, (B) $Eu(OMBA)_3$-VP-EMA and (C) $Eu(MMBA)_3$-VP-EMA.

for $Eu(BA)_3$-VP-EMA, 21.40 (613.5 nm) for $Eu(OMBA)_3$-VP-EMA and 74.43 (614 nm) for $Eu(MMBA)_3$-VP-EMA) are all stronger than the orange emission intensities of magnetic dipole transition of $^5D_0 \rightarrow {}^7F_2$ (23.89 (591 nm), 15.96 (589.5 nm) and 28.39 (590.5 nm) for $Eu(BA)_3$-VP-EMA, $Eu(OMBA)_3$-VP-EMA and $Eu(MMBA)_3$-VP-EMA, separately), indicating Eu^{3+} site in an environment without inversion symmetry [44]. Furthermore, we compared the luminescent relative intensities and lifetimes of the three hybrid polymers and their corresponding small molecular complexes, the detailed data have been listed in Table 1. Both the relative emission intensities and luminescent lifetimes of the hybrid polymer materials present apparent enhancement compared to those of complexes. The polymer chain of VP-EMA co-ordinates to Eu^{3+} ion to replace the co-ordinated water molecules generally exist in complexes of aromatic carboxylic acids, which can avoid the energy loss caused by the vibration of hydroxyl group of co-ordinated H_2O molecules. Certainly, the introduction of polymer chain forms the rigid environment to decrease the non-radiative energy loss in small molecular co-ordination compounds.

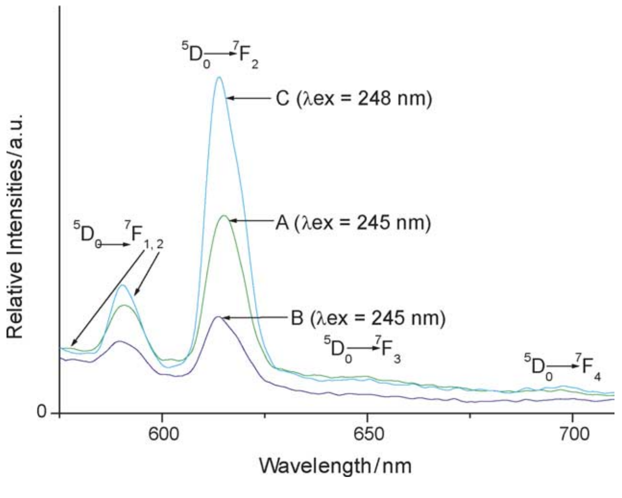

Fig. 5. Emission spectra of hybrid polymers (A) $Eu(BA)_3$-VP-EMA, (B) $Eu(OMBA)_3$-VP-EMA and (C) $Eu(MMBA)_3$-VP-EMA.

Table 1
Luminescence relative intensities and lifetimes for the hybrid polymers and corresponding small molecular complexes with aromatic carboxylic acids

Luminescent systems	Relative luminescence intensities (a.u.)	Luminescence lifetimes (μs)
$Eu(BA)_3$-VP-EMA	70.19	980
$Eu(BA)_3(H_2O)_4$	24.96	860
$Eu(OMBA)_3$-VP-EMA	38.86	1030
$Eu(OMBA)_3(H_2O)_2$	17.56	840
$Eu(MMBA)_3$-VP-EMA	107.32	1020
$Eu(MMBA)_3(H_2O)_3$	33.30	770

4. Conclusions

A novel series of Eu-containing co-polymers was prepared by the direct co-ordination co-precipitation approach among 4-vinyl pyridine units, benzoic acids (*ortho* and *meta* methylbenzoic acids) and europium ions. The co-polymers containing europium complex units exhibit a great advantage over small rare earth complexes in designing the desired conformation to sensitize the europium emission, in which the Eu–BA complexes are covalently bonded with nitrogen atoms of 4-vinyl pyridines that are not the same as general lanthanide complex-doped polymers. In addition, the resulting hybrids could be soluble in common organic solvents like butanone or acetone and can be cast into thin films with excellent mechanical flexibility and thermal stability, compared with pure lanthanide complexes. All these Eu co-polymer hybrid materials show intense red luminescence at around 614 nm, corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition under UV excitation. Consequently, we may expect that through this efficient way, the rare earth functional polymers could lead to the fabrication of high-quality color displays and be rather useful as a source of monochromatic emission in photonic crystals.

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References

[1] J.M. Lehn, Angew. Chem. Int. Ed. Engl. 29 (1990) 1304.
[2] J.C.G. Bunzli, F. Ihringer, Inorg. Chim. Acta 246 (1996) 195.
[3] P.K. Sharma, A.R. van Doom, A.G.J. Staring, J. Lumin. 62 (1994) 219.
[4] G.F. de Sa, O.L. Malta, C. de Mello Donega, A.M. Simas, R.L. Longo, P.A. Santa-Cruz, E.F. da Silva Jr., Coord. Chem. Rev. 196 (2000) 165.

[5] H. Takkalo, V.M. Mukkala, L. Merio, J.C. Rodriguez-Ubis, R. Sedano, O. Juanes, E. Brunet, Helv. Chim. Acta 80 (1997) 372.
[6] G.F. de Sa, L.H.A. Nunes, Z.M. Wang, G.R. Choppin, J. Alloys Compd. 196 (1993) 17.
[7] N. Sabbatini, M. Guardigli, J.M. Lehn, Coord. Chem. Rev. 123 (1993) 201.
[8] J.C.G. Bunzli, P. Froidevaux, J.M. Harrowfield, Inorg. Chem. 32 (1993) 3306.
[9] B. Yan, H.J. Zhang, C.G. Xu, T.L. Chen, J.Z. Ni, Spectro. Lett. 33 (5) (2000) 705.
[10] V. Tsaryuk, V. Zolin, J. Legendziewicz, R. Szostak, P. Gawryszewska, J. Alloys Compds. 380 (1–2) (2004) 418.
[11] J. Sokolnicki, J. Legendziewicz, J.P. Riehl, J. Phys. Chem. B 106 (2002) 1508.
[12] E. Huskowska, P. Gawryszewska, J. Legendziewicz, C.L. Maupin, J.P. Riehl, J. Alloys Compd. 303 (2000) 325.
[13] V. Zolin, L. Puntus, V. Kudryashova, V. Tsaryuk, J. Legendziewicz, P. Gawryszewska, R. Szostak, J. Alloys Compd. 341 (2002) 376.
[14] V. Tsaryuk, J. Legendziewicz, V. Zolin, J. Sokolnicki, R. Szostak, L. Puntus, J. Alloys Compd. 323 (2001) 661.
[15] V. Tsaryuk, I. Turowska-Tyrk, J. Legendziewicz, V. Zolin, R. Szostak, L. Puntus, J. Alloys Compd. 341 (2002) 323.
[16] V. Tsaryuk, V. Zolin, J. Legendziewicz, J. Lumin. 102 (2003) 744.
[17] Y.S. Song, B. Yan, Z.X. Chen, J. Solid State Chem. 177 (10) (2004) 3805.
[18] B. Yan, Q.Y. Xie, Montshefte Chem. 135 (7) (2004) 757.
[19] B. Yan, Y.S. Song, Z.X. Chen, J. Mol. Struct. 694 (2004) 115.
[20] B. Yan, Y.S. Song, J. Fluorescence 14 (2004) 289.
[21] B. Yan, Q.Y. Xie, Inorg. Chem. Commun. 6 (2003) 1448.
[22] B. Yan, Q.Y. Xie, J. Mol. Struct. 688 (2004) 73.
[23] L.P. Jin, S.X. Lu, S.Z. Lu, Polyhedron 15 (1996) 4069.
[24] W.M. Xue, Q.G. Wang, L. Yan, R.D. Yang, Polyhedron 11 (1992) 2051.
[25] J.F. Ma, Z.S. Jin, J.Z. Ni, Acta Cryst. C50 (1992) 1010.
[26] R.A. Chupakhina, V.V. Serebrennikov, Russ. J. Inorg. Chem. (1962) 1206.
[27] P.A. Tanner, B. Yan, H.J. Zhang, J. Mater. Sci. 35 (2000) 4325.
[28] L.R. Matthews, E.T. Knobbe, Chem. Mater. 5 (1993) 1697.
[29] H.R. Li, J. Lin, H.J. Zhang, L.S. Fu, Chem. Mater. 14 (2002) 3651.
[30] H.R. Li, J. Lin, H.J. Zhang, L.S. Fu, Chem. Commun. (2001) 1212.
[31] Q.M. Wang, B. Yan, Inorg. Chem. Commun. 7 (2004) 747.
[32] D.W. Dong, S.C. Jiang, Y.F. Men, X.L. Ji, B.Z. Jiang, Adv. Mater. 12 (2000) 646.
[33] A.C. Franville, D. Zambon, R. Mahiou, Chem. Mater. 12 (2000) 428.
[34] K. Binnemans, P. Lenaerts, K. Driesen, C. Gorller-Walrand, J. Mater. Chem. 14 (2004) 191.
[35] K. Driesen, R. Van Deun, C. Gorller-Walrand, K. Binnemans, Chem. Mater. 16 (2004) 1531.
[36] Q.M. Wang, B. Yan, Inorg. Chem. Commun. 7 (2004) 1124.
[37] Q.M. Wang, B. Yan, J. Mater. Chem. 14 (15) (2004) 2450.
[38] Y. Okamoto, J. Macromol. Sci. Chem. A24 (1987) 455.
[39] R. Iwamura, N. Higashiyama, K. Takemura, S. Tsutsumi, K. Kimura, G. Adachi, Chem. Lett. (1994) 1131.
[40] H. Chen, R.D. Archer, Macromolecules 29 (19961957).
[41] B.J. Gao, Y.F. Yang, Y. Cheng, D.J. Shi, Spectro. Spectra. Anal. 22 (2002) 371.
[42] V. Bekiari, G. Pistolis, P. Lianos, Chem. Mater. 11 (1999) 3189.
[43] L.H. Wang, W. Wang, W.G. Zhang, E.T. Kang, W. Huang, Chem. Mater. 12 (2000) 2212.
[44] Y. Hasegawa, M. Yamamuro, Y. Wada, N. Kanehisa, Y. Kai, S. Yanagida, J. Phys. Chem. A 107 (2003) 1697.