

PREPARATION AND FLUORESCENT PROPERTIES OF  $\text{Eu}^{3+}$ -CONTAINING  
CORE-SHELL NANOPARTICLES\*Zheng-hui Wang<sup>a\*\*</sup>, Li-feng Yan<sup>b</sup> and Qing-shi Zhu<sup>b</sup><sup>a</sup>Department of Chemistry, Guangzhou University, Guangzhou 510405, China<sup>b</sup>The Open Laboratory of Bond Selective Chemistry, University of Science and Technology of China, Hefei 230026, China

**Abstract** By using a two-stage soapless emulsion polymerization, four kinds of core-shell nanoparticles have been prepared, which are composed of a polystyrene core having an average diameter of 256 nm and a poly(methyl methacrylate-*co*-acrylic acid) shell. The transmission electron microscopy (TEM) micrographs and the atomic force microscopy (AFM) images evidenced the presence of a core-shell structure. In the infrared spectra, the shift of  $\nu_{\text{COOH}}$  to lower wavenumber with increasing  $\text{Eu}^{3+}$  ion content indicates that coordination between the oxygen of the carboxylic group and  $\text{Eu}^{3+}$  has occurred. The fluorescence intensity of  $^5\text{D}_0\text{--}^7\text{F}_2$  transition was observed to reach its maximum with a carboxyl group molar percentage of 40% in the shell and an  $\text{Eu}^{3+}/\text{--COO}^-$  molar ratio of 1:3. The fluorescence intensity ratio of  $^5\text{D}_0\text{--}^7\text{F}_2$  to  $^5\text{D}_0\text{--}^7\text{F}_1$  transition reached its maximum with an  $\text{Eu}^{3+}/\text{--COO}^-$  molar ratio of 1:3 for all the four series.

**Keywords** Fluorescent property,  $\text{Eu}^{3+}$ -containing nanoparticle, Soapless emulsion polymerization

## INTRODUCTION

Latex nanoparticles have potential applications in electron and nonlinear optics, optical and magnetic data storage, and chemical and biochemical sensors<sup>[1–4]</sup>. In the last decade, research on polymer nanoparticles has increased continuously<sup>[5, 6]</sup>. Polymer nanoparticles with core-shell structure were usually prepared by means of encapsulation<sup>[7]</sup>, dissolution<sup>[8]</sup> and seeded emulsion polymerization<sup>[9–10]</sup>.

By using seeded emulsion polymerization, functional polymer nanoparticles can be obtained with special design for the shell<sup>[11–14]</sup>. By introducing carboxylic group into the shell, not only can the stability of the final latex product be enhanced due to the electrostatic repulsion from the negative charges on the outer surface of the latex particles, but also the latex particles can coordinate with some metallic ions, for instance, rare earth ions.

Rare earth ions have been widely used as structure probes<sup>[15–20]</sup>.  $\text{Eu}^{3+}$  has often been used as a probe because of the simplicity of its energy-level structure. The  $^5\text{D}_0\text{--}^7\text{F}_2$  and  $^5\text{D}_0\text{--}^7\text{F}_1$  transition of  $\text{Eu}^{3+}$  are allowed by forced electric and magnetic dipole mechanism, respectively<sup>[21, 22]</sup>. Therefore, the  $^5\text{D}_0\text{--}^7\text{F}_2$  transition is very sensitive to variation of the environment of  $\text{Eu}^{3+}$  ions, and its fluorescence intensity increase as the environment becomes more symmetrical and the  $\text{Eu}\text{--O}$  covalence increases; the  $^5\text{D}_0\text{--}^7\text{F}_1$  transition is independent of that<sup>[23, 24]</sup>. The fluorescence intensity ratio of  $^5\text{D}_0\text{--}^7\text{F}_2$  to  $^5\text{D}_0\text{--}^7\text{F}_1$  can also be used as an indication of the degree of asymmetry in the vicinity of  $\text{Eu}^{3+}$  ion and  $\text{Eu}\text{--O}$  covalence<sup>[25, 26]</sup>.

Inorganic materials containing rare earth ions, such as  $\text{Eu}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Sm}^{2+}$ , have also attracted great attention as potential applications for optical devices and memory devices<sup>[27–30]</sup>. Meanwhile, materials based on polymer electrolytes modified with inorganic salts also show unique properties, which have been used for developing special devices<sup>[31, 32]</sup>. Polymeric materials doped with  $\text{Eu}^{3+}$  have important optical properties and the

\* This work was supported by the Elite Foundation of Educational Department of Guangdong Province (No. 02047).

\*\* Corresponding author: Zheng-hui Wang (王正辉), E-mail: wangzhenghui@163.net

Received March 18, 2002, Revised May 13, 2002, Accepted May 28, 2002

$\text{Eu}^{3+}$  fluorescence transition can be interpreted in terms of the composition and the local structure of the support<sup>[16, 33]</sup>.

As mentioned above, many researchers have reported functional polymer nanoparticles, but to our knowledge, there is no report on the study of fluorescent polymer nanoparticles. In this paper, we will describe the preparation and fluorescence of  $\text{Eu}^{3+}$ -doped core-shell polymer nanoparticles.

## EXPERIMENTAL

### Materials

Styrene (St), methyl methacrylate (MMA) and acrylic acid (AA) (all from Shanghai Chemical Reagent Station, China, chemical reagent grade) were distilled under reduced pressure and then stored in refrigerator before use. The initiators potassium persulfate (KPS, Aldrich, analytically pure grade) and 2,2'-azobis(2-methylpropionitrile) (AIBN, Aldrich, analytically pure grade) were used without further purification. Europium(III) oxide ( $\text{Eu}_2\text{O}_3$ , Acros Organics, 99.99%) was used as received. NaOH and HCl (from Shanghai First Chemical Plant, China, analytically pure grade) were used after dissolving or diluting to the proper concentration. Deionized water was used throughout.

### Sample Preparation

The latex core-shell particles with polystyrene core and poly(MMA-co-AA) shell were synthesized via a two-stage soapless emulsion polymerization using a semicontinuous reaction scheme. All reactions were carried out at 80°C under nitrogen in a four-necked flask fitted with a mechanical stirrer, a condenser, and two inlets for nitrogen and monomer, respectively. Prior to the addition of the initiator to start the polymerization, the flask was purged with nitrogen to remove oxygen.

### Preparation of Polystyrene Cores

120 g of water, 0.3 g of KPS and 3 g of St (about 10 wt% of the total monomer) were precharged into the four-necked flask, then heated to 80°C in an oil bath and stirred for 30 min. 27 g of St was fed into the reactor in a starve-fed regime for about 4 h. When the addition of the monomer was completed, the reaction was continued with an agitation speed of 300 rpm for another 20 h. Finally, the seed latex was obtained with a solid content of 20 wt%.

### Preparation of Latex with Poly(MMA-co-AA) Shell

25 g of the seed latex, 75 g of water and 0.005 g of AIBN were charged into the reactor, stirred for 20 min, and heated to 80°C, then 5 g of the monomer mixture, consisting of MMA and AA, was added continuously in about 3 h. Finally, the reaction was continued with an agitation speed of 320 rpm for another 10 h. In this way, we obtained four kinds of core-shell polymer particles, namely, cs-10, cs-20, cs-30 and cs-40 with AA molar percentage contents of 10%, 20%, 30% and 40% in the shell-forming monomer, respectively. In order to stabilize the core-shell particles, the reaction system must have a pH of about 8 to have the carboxyl group exposed on the surface of the growing particles or the formed particles to sustain the essential electrostatic repulsion. The pH value of the reaction system was adjusted and maintained by adding 0.2 mol/L NaOH solution.

### Coordination of $\text{Eu}^{3+}$ Ions

In order to get fluorescent material, the  $\text{Eu}^{3+}$  ions were coordinated with carboxylic groups attached on the surfaces of the obtained nanoparticles by adding  $\text{EuCl}_3$  solution to form  $\text{Eu}-\text{O}$  coordination band. We designed the experimental approach in terms of the total content of carboxylic group in the shell. By varying the molar ratio of  $-\text{COO}^-/\text{Eu}^{3+}$  from 1:1 to 1:15 for each core-shell latex particle, we obtained samples. The pH value of 10 g of core-shell latex was adjusted to 7 just before adding an appropriate amount of  $2.0 \times 10^{-2}$  mol/L  $\text{Eu}^{3+}$  ion solution. The  $\text{Eu}^{3+}$  solution was prepared by dissolving  $\text{Eu}_2\text{O}_3$  in 0.2 mol/L HCl solution and diluting with deionized water. After adding the  $\text{Eu}^{3+}$  ion solution, the mixture was stirred for 10 min for adequate coordination reaction, then centrifuged at a speed of 10000 rpm for 5 min. The sediments were dried under vacuum at 40°C for 24 h. Figure 1 demonstrated the process from core-forming to  $\text{Eu}^{3+}$ -doped particle.

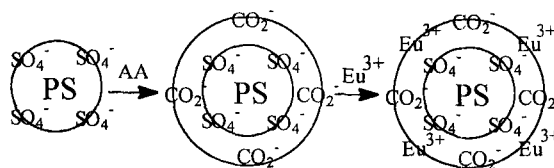


**Fig. 1** Schematic representation of the process from core-forming to  $\text{Eu}^{3+}$ -doped particle

### Characterization

The size and size distribution of the core and core-shell latex particles were investigated by TEM (Nippon Electron Inc. JEM 2010). To prepare specimens for TEM measurements, five drops of 1% phosphotungstic acid solution were added to 2 mL of the diluted latex for staining. Then one drop of the stained dilute latex was put on a Formvar-coated copper grid of 400 mesh, and dried at room temperature in a dust-free environment, then TEM micrographs were taken.

A Nanoscope IIIa AFM (Digital Instruments, USA) in tapping mode with a silicon tip was used to measure the surface morphology of the films. To prepare films, latex dispersions were poured into a cylindrical container with a flat bottom. The particles settled automatically while the water was allowed to evaporate at  $50^\circ\text{C}$ . The resonant frequency of the tip was 300.19 kHz and the cantilever length was 125  $\mu\text{m}$ . The scan rate was 2.0 Hz.

FT infrared transmission spectra were recorded with a MAGNA-IR 750 spectrometer from Nicolet Instrument Cooperation, USA, using pellets which were prepared by pressing the mixture consisting of the sample and potassium bromide. Fluorescence spectra were measured with a Hitachi 850 fluorescence spectrometer at an excitation wavelength of 394 nm at room temperature.

### RESULTS AND DISCUSSION

Figure 2 shows typical TEM micrographs of the polystyrene core and the core-shell polymer nanoparticles cs-30. The core particles have an average diameter of 256 nm. Because it is difficult to stain polystyrene nanosphere with phosphotungstic acid, all the nanoparticles appear gray with a black boundary. The core-shell nanoparticles cs-30 with an average diameter of 328 nm are black. The increase of average size and the change of the color of the stained particles provide evidence of core and core-shell structure.

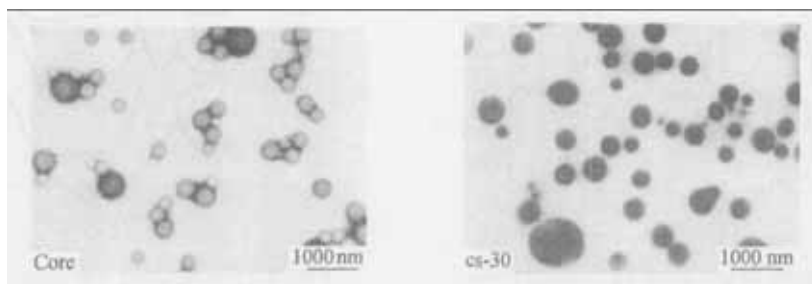


**Fig. 2** Typical TEM micrographs of core and cs-30 particles

Figure 3 shows AFM images of the core particles and the core-shell nanoparticle cs-40. From the pictures we found that the average particle size increases from the core particle to the core-shell particle, providing further evidence of the formation of core-shell structure.

Figure 4 shows the FT infrared spectra of the non- $\text{Eu}^{3+}$ -doped and  $\text{Eu}^{3+}$ -doped core-shell nanoparticles. The absorption bands at 1731, 1493, 1452, and 1241–1151  $\text{cm}^{-1}$  can be assigned as the  $\text{C}=\text{O}$  ( $-\text{COOCH}_3$ ) stretching, phenyl group skeleton,  $\text{CH}_2$  deformation and  $\text{C}-\text{O}-\text{C}$  ( $-\text{COOCH}_3$ ) stretching vibrations, respectively<sup>[34, 35]</sup>. By taking the band at 1452  $\text{cm}^{-1}$  as a reference standard, we found that there is a considerable

change of absorption bands in the region from 1673 to 1493  $\text{cm}^{-1}$ . In spectrum 1, two strong peaks at 1637 and 1560  $\text{cm}^{-1}$  are assigned to  $\nu_{\text{COOH(asy.)}}$  and  $\nu_{\text{COOH(sy.)}}$  vibrations. The  $\nu_{\text{C-C(Ar)}}$  of the phenyl group at 1602  $\text{cm}^{-1}$  is overlapped with the symmetric stretching of  $-\text{COO}^-$  and appears as a shoulder peak. With increasing  $\text{Eu}^{3+}$  ion contents, the  $\nu_{\text{COOH}}$  gradually shifts to lower wavenumbers 1643 and 1548  $\text{cm}^{-1}$ , meanwhile the  $\nu_{\text{C-C(Ar)}}$  at 1602  $\text{cm}^{-1}$  becomes more distinctive, which indicates that coordination actually occurs between the oxygen of  $-\text{COO}^-$  and  $\text{Eu}^{3+}$ . When the molar ratio of  $\text{Eu}^{3+}/-\text{COO}^-$  exceeds 1/3, the infrared spectra of cs-40 series (spectrum 5 and spectrum 6) no longer changes.

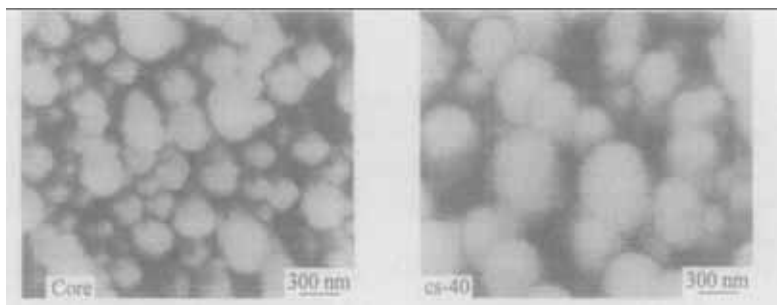


Fig. 3 Typical AFM images of core and cs-40 particles

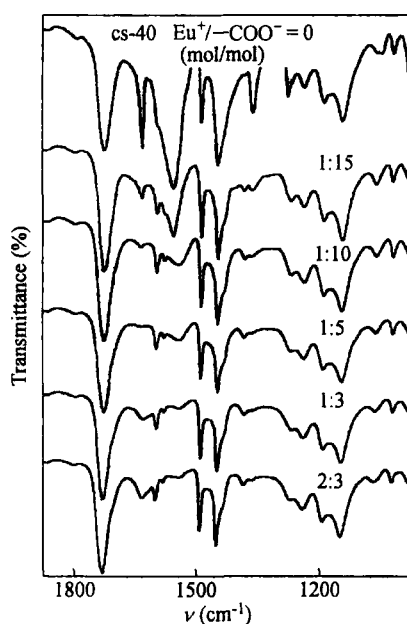


Fig. 4 IR spectra of cs-40 and  $\text{Eu}^{3+}$ -doped cs-40 series

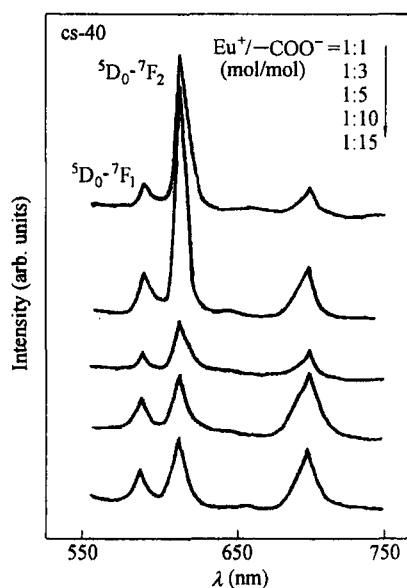


Fig. 5 Fluorescence emission spectra of  $\text{Eu}^{3+}$ -doped cs-40 series

Figure 5 shows the fluorescence emission spectra of  $\text{Eu}^{3+}$ -doped nanoparticles at different  $\text{Eu}^{3+}$  contents of the cs-40 series. The spectra were obtained using an excitation wavelength of 394 nm, which corresponds to the  $^7\text{F}_0-^5\text{L}_6$  transition<sup>[28, 36]</sup>. Taking the core-shell nanoparticles as a matrix, we can see four emission signals clearly. These signals due to  $\text{Eu}^{3+}$  are assigned to  $^5\text{D}_0-^7\text{F}_1$  (592 nm),  $^5\text{D}_0-^7\text{F}_2$  (615 nm),  $^5\text{D}_0-^7\text{F}_3$  (655 nm), and  $^5\text{D}_0-^7\text{F}_4$  (700 nm) transitions<sup>[37, 38]</sup>. But it is difficult to identify the signal from  $^5\text{D}_0-^7\text{F}_0$  (580 nm) transition, because it is very weak. The intensity of  $^5\text{D}_0-^7\text{F}_2$  transition, which is very sensitive to variation of the environment of  $\text{Eu}^{3+}$  ions due to an electric dipole transition<sup>[33]</sup>, shows a considerable change. The intensity reaches its maximum when the  $\text{Eu}^{3+}/-\text{COO}^-$  molar ratio is 1:3, which means that when the  $\text{Eu}^{3+}$  and  $-\text{COO}^-$  are equivalent, the strong  $\text{Eu}-\text{O}$

bands are formed and the environment has become symmetrical. Figure 6 indicates that the other series yield similar results. On the other hand, while the  $\text{Eu}^{3+}/-\text{COO}^-$  molar ratio is lower than 1:3, the  $\text{Eu}-\text{O}$  covalence decreases, and the intensity decreases. When the molar ratio of  $\text{Eu}^{3+}/-\text{COO}^-$  is higher than 1:3, quenching of the fluorescence will occur because of the energy transfer between the neighboring  $\text{Eu}^{3+}$  ions in the form of thermal energy.

Figure 7 shows the fluorescence intensity ratio of  ${}^5\text{D}_0\text{-}{}^7\text{F}_2/{}^5\text{D}_0\text{-}{}^7\text{F}_1$  transition of  $\text{Eu}^{3+}$ . The  ${}^5\text{D}_0\text{-}{}^7\text{F}_1$  transition is independent of the chemical environment because of its magnetic dipole transition<sup>[33]</sup> so the intensity ratio also can be used to indicate the chemical bonds in the vicinity of  $\text{Eu}^{3+}$  ions<sup>[26]</sup>. It is very significant that, when the ratio of  $\text{Eu}^{3+}/-\text{COO}^-$  is 1:3, the intensity ratios for all series almost always reach the approximate maximum simultaneously, which means the  $\text{Eu}^{3+}$  ions have a symmetric chemical environment and strong  $\text{Eu}-\text{O}$  bands are formed. It is very interesting to note that when the ratio is 1:15, the intensity ratios for the four series reach the approximate minimum, which may be attributable to the minimum of the covalence of  $\text{Eu}-\text{O}$  in the samples.

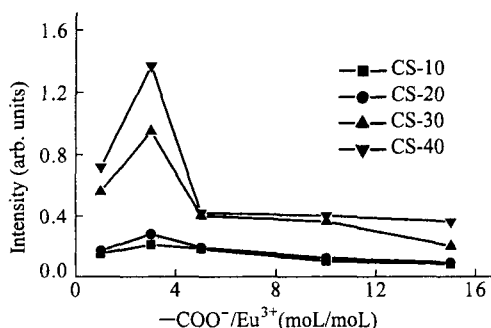


Fig. 6 Relationship between fluorescence intensity and the molar ratio of  $-\text{COO}^-/\text{Eu}^{3+}$  for all the four series

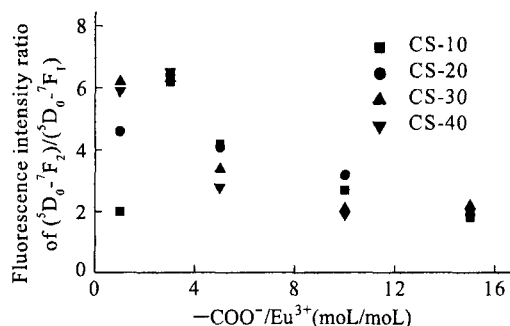


Fig. 7 Relationship between fluorescence intensity ratio of  $({}^5\text{D}_0\text{-}{}^7\text{F}_2)/({}^5\text{D}_0\text{-}{}^7\text{F}_1)$  and molar ratio for all the four series

## CONCLUSION

With a two-stage soapless emulsion polymerization, we have prepared the core-shell polymer nanoparticles. The core latex particles were stabilized by the ion fragments from the ionic initiator. The core-shell latex particles were stabilized by the electrostatic repulsion from the carboxylic group introduced in the shells. The size and size distribution and morphology of all the particles were directly investigated with TEM and AFM.

By studying the infrared spectra of  $\text{Eu}^{3+}$ -doped nanoparticles, evidence was found that coordination occurred between  $\text{Eu}^{3+}$  ion and carboxylic group on the outer surface of the nanospheres.

Using an excitation wavelength of 394 nm, the fluorescence spectra of  $\text{Eu}^{3+}$ -doped samples were obtained. The fluorescence intensity of  ${}^5\text{D}_0\text{-}{}^7\text{F}_2$  transition and the fluorescence intensity ratio of  ${}^5\text{D}_0\text{-}{}^7\text{F}_2$  to  ${}^5\text{D}_0\text{-}{}^7\text{F}_1$  transition reach a maximum for all the four series when the  $\text{Eu}^{3+}/\text{COO}^-$  molar ratio is 1/3, which means that, when the  $\text{Eu}^{3+}$  and  $-\text{COO}^-$  are equivalent, the vicinity of  $\text{Eu}^{3+}$  ions is symmetrical and strong  $\text{Eu}-\text{O}$  bonds are formed at this molar ratio.

## REFERENCES

- Olga, K. and Eugenia, K., *Macromolecules*, 1999, 32: 4122
- Holland, B.T., Blandford, C.F. and Stein, A., *Science*, 1998, 281: 538
- Wijnhoven, J.E.G.J. and Vos, V.L., *Science*, 1998, 281: 802
- Tse, A.S., Wu, Z. and Asher, S.A., *Macromolecules*, 1995, 28: 6533
- Fritz, H., Maier, M. and Bayer, E.J., *Colloid Polym. Sci.*, 1997, 195: 272
- Muler, J.J., Lukowski, G., Krober, R., Damuschun, G. and Dittgen, M., *J. Colloid Polym. Sci.*, 1994, 272: 755

- 7 McDonald, C.J., Bouck, K.J., Chaput, A.B. and Stevens, C.J., *Macromolecules*, 2000, 33: 1593
- 8 Okubo, M., Sugiiura, R., Fukami, N. and Ito, A., *Colloid and Polym. Sci.*, 1997, 275: 170
- 9 Park, J.G., Kim, J.Y. and Sui, K.D., *J. Appl. Polym. Sci.*, 1998, 69: 2291
- 10 Slawinski, M., Schellekens, M.A.J., Meuldijk, J., Herk, A.M.V. and German, A.L., *J. Appl. Polym. Sci.*, 2000, 76: 1186
- 11 Lous, M., Sparnacci, K., Lelli, M., Vannini, R. and Tondelli, L., *J. Polym. Sci., Part A: Polym. Chem.*, 2000, 38: 1110
- 12 Perez, N., Whitcombe, M.J. and Vulfson, E.N., *J. Appl. Polym. Sci.*, 2000, 77: 1851
- 13 Wang, Y., Feng, L. and Pan, C., *J. Appl. Polym. Sci.*, 1998, 70: 2307
- 14 Okube, M., Ahmad, H. and Komura, M., *Colloid Polym. Sci.*, 1996, 274: 1181
- 15 Yen, W.M., *Laser Spectroscopy of Solid*, Springer, Berlin, 1981
- 16 O'Kelly, B., Tang, Z.R. and Mcgilp, J.F., *J. Non-cryst. Solids*, 1992, 147-148: 97.
- 17 Wolfson, J.M. and Kearns, D.R., *Biochem.*, 1975, 14: 1436
- 18 Kido, J., Brittain, H.G. and Okamoto, Y., *Macromolecules*, 1988, 21: 1872
- 19 Barela, T.D., Burchett, S. and Kizer, D.E., *Biochem.*, 1975, 14: 4887
- 20 Djordjeric, C. and Craig, S.A., *Inorg. Chem.*, 1985, 24: 1283
- 21 Jorgensen, C.K. and Judd, B.R., *Molec. Phys.*, 1964, 6: 281
- 22 Peacock, R.P., *Struct. Bonding*, 1975, 22: 83
- 23 Oomen, E.W.J.L. and Dongen, A.M.A.V.J., *Non-cryst. Solids*, 1989, 111: 205
- 24 Tanabe, S., Ohyagi, T., Soga, N. and Hanada, T., *Phys. Rev. B*, 1992, 46: 3305
- 25 Gallagher, P.K., *J. Chem. Phys.*, 1964, 41: 3061
- 26 Capobianco, A., Proulx, P.P., Bettinelli, M. and Negrisola, F., *Phys. Rev. B*, 1990, 42: 5936
- 27 Toratani, H., Izumitani, T. and Kuroda, H., *J. Non-cryst. Solids*, 1982, 52: 303
- 28 Nageno, Y., Takebe, H. and Morinaga, K., *J. Non-cryst. Solids*, 1994, 169: 288
- 29 Jaaniso, R. and Bill, H., *Europhys. Lett.*, 1991, 16: 569
- 30 Tanaka, M. and Kushida, T., *Phys. Rev. B*, 1994, 49: 5192
- 31 Fujiinami, T., Metha, M.A., Yamada, Y., Hiramatsu, M. and Hirano, I., *J. Polym. Sci. B: Polym. Phys.*, 1997, 35: 2057
- 32 Puga, M.M.S., Carlos, L.D., Arrantes, T. M. A. and Alcacer, L., *Electrochim. Acta*, 1995, 40: 2383
- 33 Nogami, M. and Abe, Y., *J. Non-cryst. Solids*, 1996, 197: 73
- 34 Dong, J., Ozaki, Y. and Nakashima, K., *J. Polym. Sci. B: Polym. Phys.*, 1997, 35: 507
- 35 Hu, H., Saniger, J., Garcia-Alejandre, J. and Castano, V.M., *Mater. Lett.*, 1991, 12: 281
- 36 Flores, M., Rodriguez, R. and Arroyo, R., *Mater. Lett.*, 1999, 39: 329
- 37 Carlos, L.D., Assuncao, M. and Alcacer, L.J., *Mater. Res.*, 1995, 10: 202
- 38 Clement, R., Leanstic, A. and Francis, A.H., *J. Phys. Chem.*, 1991, 95: 5404