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Synthesis and fluorescence properties of terbium-calcium-PMDMBA ①

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Abstract: A novel rare earth complex monomer Tb-Ca-PMDMBA (PMDMBA denotes pyromellitic dianhydride-modified Bisphenol A epoxy acrylate resin) was synthesized for the first time as following procedure. Firstly, Bisphenol A epoxy acrylate resin and Bisphenol A epoxy acrylate resin modified with pyromellitic dianhydride were synthesized from Bisphenol A epoxy resin, acrylic acid and pyromellitic dianhydride through esterification respectively. Their composition is ascertained by the analysis of acidic value and FTIR spectrum. Secondly, the complex monomer Tb-Ca-PMDMBA was prepared by coordinating Tb^{3+}, Ca^{2+} with carboxyl groups, and then its fluorescence properties were investigated. The results show that Tb-Ca-PMDMBA complex can emit intense characteristic emission spectrum of Tb^{3+} ion under UV excitation. The fluorescence intensity depends on the content of Tb^{3+} and reaches maximum when the mole ratio of Tb to Ca is 2∶9.

Key words: terbium fluorescence; complex monomer; fluorescence enhancement; modification
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1 INTRODUCTION

In recent years, many investigations on fluorescence properties of rare earth ions-containing polymer complexes have been made because the polymers can be used as luminescence and laser materials with good quality[1-5]. Okamoto et al[6-8] synthesized polymers containing coordination groups and studied their fluorescence properties. However, the synthesis of functional groups polymers with good energy doner and energy level matching capability was very complicated, which made the use of polymer luminescent materials uneconomic[1]. Furthermore, the direct reaction of rare earth ions with polymer ligands usually formed low coordination number complexes and ions aggregates[8], which resulted in the weaker fluorescence emission of complexes. So, recently some of complex monomers with coordination functional groups which could coordinate with RE-ions to form good fluorescence materials were synthesized. And a new type of polymer functional fluorescence material was prepared through polymerization or co-polymerization. A survey of the literature shows that present research mostly focused on methyl methacrylate and acrylic acid. However, little attention has been paid to synthesis, characterization of RE-aromatic acid modified epoxy complexes.

Since rare earth-aromatic carboxylic acid complexes had many special structures and properties, many of them were synthesized, characterized, and applied to practical application[9, 10]. For example, agriculture films by intermingling with rare earth-aromatic carboxylic acid complexes could gain output of cropper. However, the poor solubility of RE-complex compounds in solvent and low consistency with polymer limited their practical application.

Epoxy compounds could carry out many modifications due to high active epoxy groups. For example, many kinds of esters would be prepared through epoxy compounds with carboxylic acid or anhydride reaction[11, 12].

Therefore, the aim of our study is to synthesize RE-active monomer to which aromatic carboxylic acids are attached and to investigate their fluorescent properties. This study is very important for the synthesis of new functional polymer material containing RE-ion and for the potential application in the field of fluorescence and laser systems.

2 EXPERIMENTAL

2.1 Reagents and materials

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Tb_4O_7(99.9%) was purchased from the Hunan Rare Earth Metals Institute. E-51 epoxy resin(epoxy equivalent 192) was purchased from Yue-yang Chemical Factory, Hunan province. Pyromellitic dianhydride, acrylic acid, hydrochloric acid, sodium hydroxide, N, N-dimethylbenzylamine and p-hydroxyanisol were all analytically pure.

2.2 Preparation

2.2.1 Synthesis of Bisphenol A epoxy acrylate resin (EA)

E-51 epoxy resin (384.0 g) and p-hydroxyanisol (0.3 g) were put in four-necked round-bottom flask with reflux exchanger, dripping funnel, thermometer and stirrer. The mixture of 137.3 g acrylic acid(the molar ratio of acrylic acid to epoxy functional group was 1∶1) and 4.05 mL N, N-dimethylbenzylamine were dropped into the flask through dripping funnel under the protection of nitrogen and stirred and refluxed at (90 ±5) ℃ for 4 - 5 h. The esterification was carried out under the optimum conditions. The reaction ended when the acidic value was less than 5 mg/g. The data of acidic value and relevant IR spectrum were listed in the Table 1 and Table 2, respectively. The sample was white or buff. EA structure could be schematically described, as shown in Fig. 1.

Table 1 Change of acidic value with time

Time/h	A*	B*
0.0	212.4	465.6
0.5	156.0	–
1.0	124.0	371.2
2.0	69.2	358.2
3.0	42.5	352.6
4.0	27.3	350.6
5.0	17.4	351.2
5.5	12.4	350.0
6.0	6.5	–
6.5	4.7	348.44* *

* * Datum is theoretical acidic value in final point of reaction

A* : acidic value of reaction mixturn during process of synthesis EA;

B* : acidic value of reaction mixturn during process of synthesis PMDMBA

2.2.2 Synthesis of Bisphenol A epoxy acrylate resin modified with pyromellitic dianhydride(PMDMBA)

Pyromellitic dianhydride (3 200 mg, 14.67 mmol) was put in a 150 mL three-necked flask with reflux condenser and drop-funnel, then dissolved in 30.0 mL acetone. The acetone solution of Bisphenol A epoxy acrylate resin(3 872 mg, equal to 14.63 mmol hydroxyl group) mixed with a little of catalyst N, N-dimethylbenzylamine and polymerization-retarder p-hydroxyanisol in 20.0 mL acetone was dripped to the flask, then the mixture was stirred and refluxed at 50 ℃ for 4 - 5 h. The reaction ended when acidic value reached theoretic acidic value. The data of acidic value and IR spectrum (sample for IR measurement was purified twice in acetone solution and dried in vacuum) were listed in Table 1 and Table 2, respectively. PMDMBA was shown schematically in Fig. 2.

The sample was cooled down to room temperature, and then neutralized by adding stoichiometrically amount of aqueous solution of sodium hydroxide.

2.2.3 Synthesis of Tb-Ca-PMDMBA complexes

A measured amount of Tb_4O_7 was weighted precisely and dissolved in concentrated hydrochloric acid and excessive hydrochloric acid was vaporized out. The obtained solution was 0.20 mol/L aqueous solution of terbium chloride. According to the general formula $Tb_{(1-x)}Ca_x\,PMDMBA_{(3-x)/6}$ (x denotes mole fraction of Ca), a series of samples were prepared. For a typical preparation process, 20 mL solution containing 4 mmol terbium chloride and 15 mmol calcium chloride were gradually dripped to PMDMBA acetone/aqueous solution(containing 7 mmol PMDMBA) at 50 - 55 ℃. The mixture was then stirred for 4 h with magnetic stirrer. The deposit was washed with acetone aqueous solution and distilled water successively, then dried in vacuum at 55 ℃ for 48 h. The sample was pure white powder.

In order to compare with Tb-Ca-PMDMBA complexes, Tb-PMA (PMA denotes pyromellitic acid) was prepared according to Ref. [13].

2.3 Apparatus

Model F-2500 FL spectrophotometer was used to record excitation and emission spectrum of complexes. IR spectrum was measured on FTIR-8300 spectrophotometer(SHIMADU DZU). Acidic value was determined through the method of chemical analysis[14].

3 RESULTS AND DISCUSSION

3.1 Composition of samples

As Bisphenol A epoxy resin did not have definite molecular formula, analysis of acidic value and IR spectrum was used as a means of determination of samples.

Bisphenol A epoxy acrylate resin (EA) was ascertained by the change of acidic value of the reaction mixture and further identified by IR spectra (as shown in Table 1 and Table 2, respectively), Table 1 shows that acidic value A* get to be smaller and smaller with the reaction going on, indicating that the reaction is ended according to the es-

Table 2 Assignments of main characteristic FTIR absorption peaks of samples (cm^{-1})

Sample	Anhydride	$\nu_{(OH)}$	- COOH		- COOR	- COO-		$\nu_{(C=C)}$	epoxy-group	
	- CO- O- CO-		$\nu_{(OH)}$	$\nu_{(-C=O)}$	$\nu_{(-C=O)}$	ν_{as}	ν_s		ν_{as}	ν_s
1		3502							916	1245
2			2 993	1 703				1 635		
3		3 490			1 714			1 633		
4	1 282 1 714				1 714					
5		3 421			1 726	1 560	1 508			

1 —Bisphenol A epoxy resin; 2 —Acrylic acid; 3 —EA; 4 —PMDMBA; 5 —Tb-Ca-PMDMBA

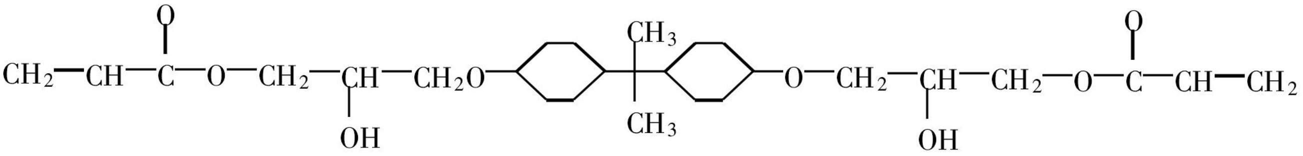

Fig. 1 EA schematic struction

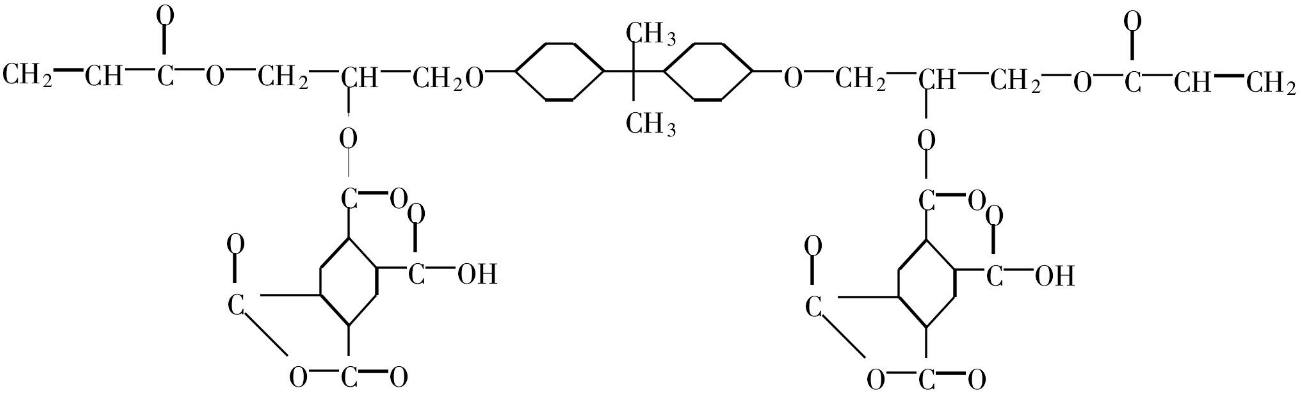

Fig. 2 PMDMBA schematic structure

terification theory when acidic value is smaller than 5 mg/g (KOH/sample)[14]. All characteristic vibrational absorption peaks of EA are listed in Table 2, including strong broad absorption peaks of hydroxyl-groups and carboxyl group stretching vibration (ν_{O-H} 3 417 cm^{-1}, $\nu_{C=O}$ 1 714. 6 cm^{-1} respectively), and bend vibration absorption peak of C= C- H ($\nu_{C=C-H}$ 983 cm^{-1}). Furthermore, the characteristic absorption of epoxy group at 916. 1 cm^{-1} disappeared. All the above results show that EA was synthesized.

Pyromellitic diandihydride modified EA is ascertained by the change of acidic value in the reaction mixture (listed in Table 1). It can be seen from Table 1 that the acidic values B^* of the mixture get to be smaller and smaller with the reaction going on, finally it is invariable basically and is consistent with calculated value, which suggests that PMDMBA has been prepared by comparison with result of theoretical value according to esterification reaction theory. In the Table 2, characteristic absorption peaks of anhydride at 1 782. 1 cm^{-1} and 1 714. 5 cm^{-1} (asymmetric and symmetric stretching vibration absorption of carboxyl groups) respectively indicate that PMDMBA was synthesized.

From Table 2, the characteristic FTIR wavenumbers of Tb-Ca-PMDMBA appeared at 1 560 cm^{-1} and 1 508 cm^{-1}, and they are attributed to the asymmetry and symmetry stretching vibration absorption of - COO- in the complexes respectively. In addition, in Fig. 3, excitation spectrum exhibits a broad band ranging from 250 nm to 350 nm with the maximum excitation wavelength at 319 nm. The results indicate that Tb-Ca-PMDMBA complex was formed[15].

3. 2 Excitation and emission spectra as well as energy transfer process of Tb-Ca-PMDMBA complex system

The excitation spectra of Tb-Ca-pyromellitic acid and Tb-Ca-PMDMBA are shown in Fig. 3. The excitation spectra of all Tb-Ca-PMDMBA complexes which includes a broad band peak (excitation peak of ligand 280 - 330 nm) and weaker narrow peaks (situated at 260 - 280 nm, characteristic excitation of

Tb^{3+} ion) as well as weaker narrow peaks at 350 - 400 nm are similar to those of Tb-Ca-PMA. The maximum excitation wavelength of Tb-Ca-PMDMBA complexes shifted toward longer wavelengths with the increase of calcium ion content, and the absorption intensity dropped more slowly than Tb-Ca-pyromellitic acid. Within the range of x from 0 to 1, the maximum excitation wavelengths shifted toward long wavelength with 20 nm. The emission spectra of all Tb-Ca-PMMBEA complexes, excited at maximum excitation wavelength, all emitted strong fluorescence typical of Tb^{3+} ion. The emission lines centered at 485, 545, 585, 622 nm are attributed to the ${}^5D_4 \rightarrow {}^7F_6$, ${}^5D_4 \rightarrow {}^7F_5$, ${}^5D_4 \rightarrow {}^7F_4$, ${}^5D_4 \rightarrow {}^7F_3$ transition in Tb^{3+} ion respectively. The emission centered at 545 nm is the strongest. The emission fluorescence assignments as well as relative intensity of Tb-Ca-PMMBEA complexes containing different Ca^{2+} mole fraction x are listed in Table 3. Table 3 shows that luminescent intensity of Tb-Ca-PMDMBA complex became greater with the increase of the mole ratio of Ca to Tb and reached maximum when the mole ratio was 9/2, and then decreased with increasing the mole ratios continuously. Fig. 4 shows the typical emission spectrum of Tb-Ca-PMDMBA. Though the fluorescence intensity of Tb-Ca-PMDMBA complex systems changed sharply with the change of the mole fraction x, their emission wavelength remained unchanged basically, which shows the characteristic emission of Tb^{3+} ion and an efficient energy transfer progress from ligand to Tb^{3+} ion. It is known that emission intensity is relevantto two states: the triplet of ligand and resonance energy level of RE-ions. Firstly, the energy absorbed by ligand under ultraviolet light is transferred to the single level and then to excited triplet of ligand through systemcrossing. The resonance level of RE-ions obtained energy from the excited triplet of ligand, and came back ground level through emitting fluorescence. It is worth noting that the maximum fluorescence intensity of Tb-Ca-PMDMBA appeared when the mole ratio of Ca to Tb was 9∶2. However in Tb-Ca-PMA complex, the maximum fluorescence was attained with the mole ratio of 4∶1, which suggests that the coordination environment around Tb-ion has great effects on the fluorescence intensity of the complex.

In addition, the preliminary study showed that the monomer complex (Tb-Ca-PMDMBA complex) had better dispersibility in 2-hydroxy methyl propionate modified Toluene-2, 4-diisocyanate and could also dissolve in mixture of Bisphenol A epoxy acrylate resin and TPGDA. The copolymer of the former would emit intensive fluorescence; while the later made the fluorescence out completely due to high energy vibration of hydroxyl groups.

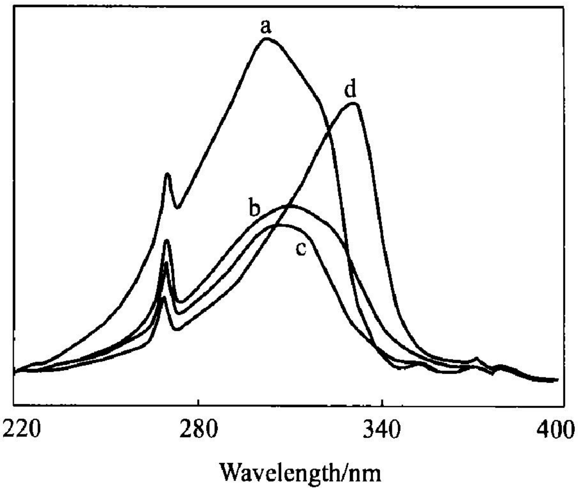

Fig. 3 Excitation spectra of Tb-Ca_4-$PMA_{11/4}$(a); Tb-Ca_4-$PMDMBA_{11/6}$(b); Tb-$PMDMBA_{1/2}$(c) and Tb-Ca_{10}-$PMDMBA_{23/6}$(d)

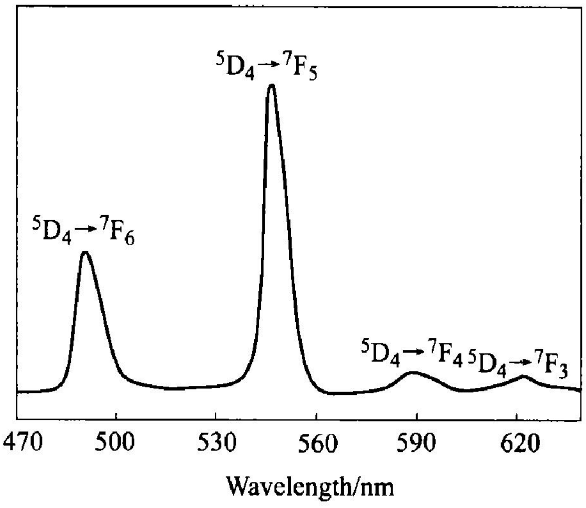

Fig. 4 Typical emission of Tb-Ca_{10}-$PMDMBA_{23/6}$

Table 3 Emission band assignments and relative intensity of Tb^{3+} ion with different Ca contents in Tb-Ca-pyromellitic acid and Tb-Ca-PMDMBA complexes

Complex	$5^{D}_{4} \rightarrow {}^7F_6$		${}^5D_4 \rightarrow {}^7F_5$		${}^5D_4 \rightarrow {}^7F_4$		${}^5D_4 \rightarrow {}^7F_3$	
	λ_{em}/nm	I_1/(a.u)	λ_{em}/nm	I_2/(a.u)	λ_{em}/nm	I_3/(a.u)	λ_{em}/nm	I_4/(a.u)
a	491.0	2.03	547.5	6.89	586.0	0.30	622.5	0.01
b	491.0	1.02	546.0	2.25	586.0	0.12		
c	491.0	0.93	546.0	1.95	586.0	0.12		
d	490.0	1.98	546.0	4.29	585.0	0.25	623.5	0.13
e	491.0	2.62	546.0	6.06	586.0	0.30	623.5	0.20

(a) Tb-Ca_4-$PMA_{11/4}$; (b) Tb-Ca_4-$PMDMBA_{11/6}$; (c) Tb-$PMDMBA_{1/2}$; (d) Tb-Ca_{10}-$PMDMBA_{23/6}$; (e) Tb_2-Ca_9-$PMDMBA_4$.

4 CONCLUSIONS

1) Bisphenol A epoxy acrylate resin (EA) and pyromellitic dianhydride modified Bisphenol A epoxy acrylate resin (PMDMBA) are synthesized from raw material Bisphenol A epoxy resin and acrylic acid.

2) Tb-Ca-PMDMBA complexes are synthesized and their properties are investigated, which indicates that the complexes can emit the characteristic fluorescence of Tb^{3+} ion and exhibit an effcient energy transfer progress from ligand PMDMBA to Tb^{3+} ion.

3) Tb-Ca-PMDMBA complexes can emit strong fluorescence and the fluorescence intensity of Tb-Ca-PMDMBA complexes becomes greater with the increase of calcium ion content and reaches to maximum when the mole ratio of Tb to Ca is 2∶9.

REFERENCES

[1] WANG Yun-pu, LEI Zi-qiang, FENG Han-yu, et al. Synthesis and fluorescence properties of RE metal ion-polymer ligand-low molecular weight ligand ternary complexes[J]. J App Poly Sci, 1992, 45 (9): 1641 - 1642.

[2] DU Chen-xia, XU Yan, MA Lin, et al. Synthesis and fluorescence properties of europium-polymer complexes containing naphthoate ligand[J]. J Alloys Comp, 1998, 265 (1 - 2): 81 - 86.

[3] LU Hong, LI Gao-fen, FANG Shi-bi, et al. Fluorescence properties of polymer-rare ion complexes. Ⅱ. Poly (acrylic acid-co-acrylamide) rare earth ion complexes[J]. J App Poly Sci, 1990, 39(6): 1389 - 1398.

[4] XU Wen-ying, WANG Yue-sheng, ZHENG Da-gang, et al. Synthesis and characterization of polymers containing rare earth metal[J]. J Macro Sci Chem, 1988, A25(10 - 11): 1397 - 1406.

[5] Li W L, Taka Y, Mishima. The fluorescence of transparent polymer films of rare earth complexes[J]. Inorg Chim Acta, 1986, 121 (1): 97 - 101.

[6] Ueba Y, Banks E, Okamoto Y. Investigation on the synthesis and characterization of rare earth metal-containing polymers —2. Fluorescence properties of Eu^{3+}-polymer complexes containing β-diacetone ligand[J]. J App Poly Sci, 1980, 25 (9): 2007 - 2017.

[7] Banks E, Okamoto Y, Ueba Y. Synthesis and characterization of rare earth metal-containing polymers —1. Fluorescence properties of ionomers containing Dy^{3+}, Er^{3+}, Eu^{3+}, and Sm^{3+} [J]. J App Poly Sci, 1980, 25(3): 359 - 368.

[8] Okamoto Y, Ueba Y, Dzhanibekov N F. Characterization of ion-containing polymer structures using rare earth metal florescence probes[J]. Macromolecules, 1980, 14: 17 - 25.

[9] WANG Zhe-min, CAO Jin-rong, CHEN Zhi-rong, et al. Study on terbium-doped polypropyrene film[J]. Journal of the Chinese Rare Earth Society, 1998, 16(4): 315 - 318. (in Chinese)

[10] WEN Yao-xian, WEN Yong, WANG Ze-min. Study on polypropyrene film doped with europium[J]. Chinese Rare Earth, 1998, 19(2): 33 - 35. (in Chinese)

[11] XU Li-zhen, SHI Li-ping. Development of epoxy modified acrylic coating[J]. Coating Industry, 1998(6): 16 - 18. (in Chinese)

[12] CHU Heng, WANG Yan-wu, LI Chun-qing. Development of UV curable epoxy acrylate coating[J]. Journal of Wuhan Institute of Chemical Technology, 1999, 21 (3): 17 - 19. (in Chinese)

[13] ZHAO Xue-hui, MAO Xiang-hui, LIAN Shi-xun, et al. An approach to the fluorescence feature of Tb^{3+}-pyromellitic acid-Ca^{2+} and its mechanism [J]. Journal of Yiyang Teachers College, 1998, 15(5): 30 - 32. (in Chinese)

[14] CHU Heng, WANG Yan-wu, LI Chun-qing. UV-curing epoxy acrylate coating[J]. Coating Industry, 1999 (10): 3 - 4. (in Chinese)

[15] MENG Qing-guo, ZHENG Hong-jie, WANG Shu-bin. Preparation and characterization of luminescent thin doped with rare earth (Tb^{3+}, Eu^{3+}) complexes derived from a sol-gel progress[J]. Materials Letters, 2000, 45: 213 - 216.

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