A New Way to Construct Luminescent Functionalized Polysiloxane Based on Ternary Lanthanide Complexes of 1, 10-Phenanthroline

Haifeng Lu, Lei Liu, Shengyu Feng

Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, People's Republic of China

ABSTRACT: A kind of polysiloxane with ester group as the functional side chain was prepared via hydrosilylation reaction in this article. Then the functionalized polysiloxane was submitted to complex with 1, 10-phenanthroline and lanthanide ions (Tb^{3+} and Eu^{3+} ions, respectively) to obtain two luminescent functionalized polysiloxanes. The molecular energy transfer process takes place within these systems in terms of sensitized functions of 1, 10-phenanthroline. Narrow-width green and red emissions were achieved. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1884–1888, 2012

Key words: luminescence; polysiloxane; polymer synthesis; characterization

INTRODUCTION

The polysiloxane has many specific properties such as good water repellency, lubricity, high flexibility of main chains, low variation of viscosity with temperature and physiological inertness, and excellent thermal stability.[1,2] So the functionalized polysiloxane can be used in a wide range of applications such as coating, adhesives, impact-resistance plastics, etc.[3–6] Recently, some studies have focused on the performance of the system of polysiloxane and acrylic monomers.[7,8] Some researches have mentioned that the silicone-acrylic graft copolymers containing cationic groups can enhance the wash fastness of the dyed fabric and not affect the fabric handle.[8–10] Then the functionalized polysiloxane is investigated as potential phosphors in organic light emitting materials by the combination of luminescent group.

Lanthanide complexes have been researched thoroughly as practical luminescent materials in view of their long-lived excited-states characteristic and their especially efficient strong narrow-width emission bands in the visible region.[11] But the lanthanide complexes' poor mechanical properties limit their uses as luminophor. The common solution is to entrap lanthanide complexes in various hosts whose structure could show good properties.[12–16]

So combining the functionalized polysiloxane and the lanthanide complexes via coordination may utilize both of their outstanding properties. The organic groups can reinforce the energy absorbability with chromophoric group and the energy can be transferred to the lanthanide ions efficiently.[17] This mechanism is called the antenna effect.[18] And the main chain of polysiloxane could offer the excellent chemical and physical performance.

In this article, we describe the preparation of luminescent functionalized polysiloxane (LFPS) based on ternary lanthanide complexes of 1, 10-phenanthroline. Ester functionalized linear polysiloxane of the type $Me_3SiO(MeRSiO)_x(Me_2SiO)_ySiMe_3$ was synthesized by the modification of poly(methylhydridosiloxane), $Me_3SiO(MeSi\{H\}O)_x(Me_2SiO)_ySiMe_3$. Methyl methacrylate could be incorporated as side-arm substituent on the polymer backbone using this methodology.[19] The derived multifunctionalized polysiloxane was afterward submitted to complex with 1,10-phenanthroline and lanthanide ions to obtain the luminescent materials. The luminescence behavior of the LFPS was compared with those of the pure complexes $Ln(NO_3)_3$ and $[Ln(phen)_3](NO_3)_3$ (Ln = Eu or Tb). This work is a continuation of our precious studies on functionalized polysiloxane,[20] and we wished to generate a general procedure that could be used to synthesize luminescent polysiloxane materials with different loading of various functional groups.
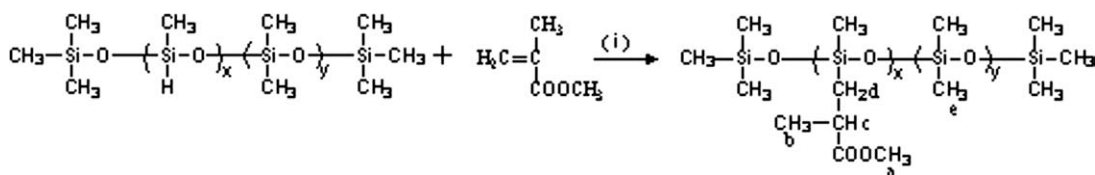
Scheme 1 The preparation of ether functionalized linear polysiloxanes (i) N_2, reflux, catalyst, 4d, 70°C.

EXPERIMENTAL SECTION

Chemicals and procedures

Starting materials and solvents were purchased from China National Medicines Group and were distilled before utilization according to the literature procedures.[21] Europium and terbium nitrates were obtained from the corresponding oxides in dilute nitric acid.

The typical procedure for the preparation of ester functionalized polysiloxane (EFPS) was described in Scheme 1 according to the reference.[22,23] Methyl methacrylate (50 mmol) and poly(methylhydrosiloxane) (PMHS) (The molecular weight is 3000 and H content of polysiloxane is 0.1%) (1 mmol) were placed in a flask with dry toluene (60 mL) and heated to 70°C under N_2, then four drops of the catalyst, namely platinum-divinyltetramethyldisiloxane complex, were added. The resultant mixture is then stirred for nearly 4 days. Removal of the solvent in vacuum and subsequent reflux in MeOH resulted in the siloxane product. Polymethylmethacrylate (PMMA) residue is removed by dissolving the product in hexane, followed by filtration or centrifugation of the solution (PMMA is not soluble in hexane). After isolation, transparent oil (named ester-functionalized polysiloxane in this article) was obtained. 1H NMR (CDCl3): δ 3.65(3H, s, a), 2.60(1H, m, c), 1.20(3H, d, b), 0.74(2H, d, d), and 0.05(81H, s, e).

The LFPS was prepared as follows: the ethanol solution of lanthanide nitrate (europium and terbium nitrate, respectively) was added with the molar ratio 1 : 1 of $Ln(NO_3)_3 \bullet 6H_2O$ to ester-functionalized polysiloxane (EFPS) under stirring. Then the ethanol solution of 1,10-phenanthroline (phen for short) was put into the mixture gradually (phen:Ln = 3 : 1). The mixture was agitated magnetically to achieve a single phase for 4 h. The desired complex was dried under vacuum at room temperature. It was named LFPS-europium (LFPS-E) when made from EFPS, europium nitrate and phen. And it was LFPS-terbium (LFPS-T) when made from EFPS, terbium nitrate, and phen.

The lanthanide complex $[Eu(phen)_3](NO_3)_3$ or $[Tb(phen)_3](NO_3)_3$ was prepared as follow: 10-mL ethanol solution (0.01 mol L^{-1}) of Eu(NO3)3•6H₂O (or Tb(NO3)3•6H₂O) was added into 30-mL ethanol solution of 1,10-phenanthroline (0.01 mol L^{-1}) under

stirring. The mixture was agitated magnetically for one hour. Then the precipitates were collected by filtration. The solids were washed with methanol and were dried under vacuum at room temperature.

Measurements

Fourier transform infrared (FTIR) spectra were measured within the 4000–400 cm^{-1} region on a Bruker TENSOR27 infrared spectrophotometer with the KBr pellet technique. ^1H NMR spectra were recorded in CDCl₃ on a BRUKER AVANCE-300 spectrometer without inter reference. Luminescence (excitation and emission) spectra of solid complexes were determined with a Perkin-Elmer LS-55 spectrophotometer whose excitation and emission slits were 10 and 5 nm, respectively.

RESULTS AND DISCUSSION

The FTIR spectra for methyl methacrylate (a), PMHS (b), and the functionalized polysiloxane (c) are shown in Figure 1. In the curve of methyl methacrylate (a), the ν(C=C) vibration was observed at 1630 cm^{-1} and the ν(C=C–H) vibration was clearly appeared at 2990 cm^{-1}.[24] They all disappeared in the curve of functionalized polysiloxane (c), indicating that the hydrosilylation reaction finished completely and no residual methyl methacrylate existed in the functionalized polysiloxanes. Compared with the curve of PMHS (b), the ν(C=O) vibration mode
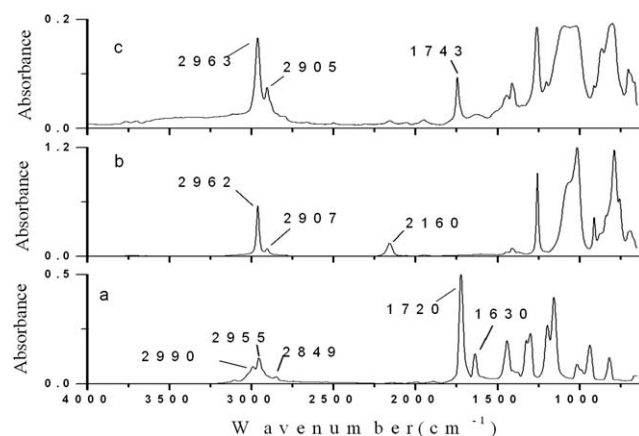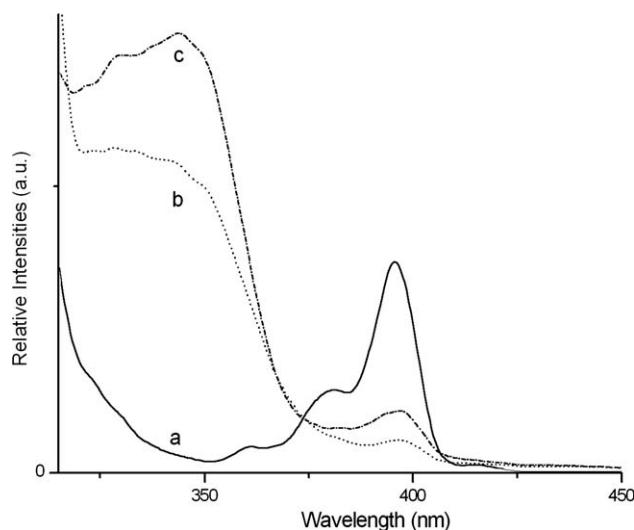

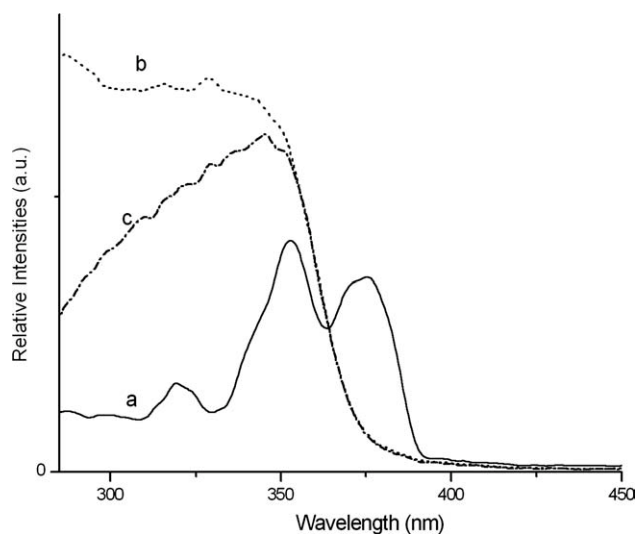**Figure 1** Infrared spectra of methlmethacrylate (a), PMHS (b), and the functionalized polysiloxane (c).
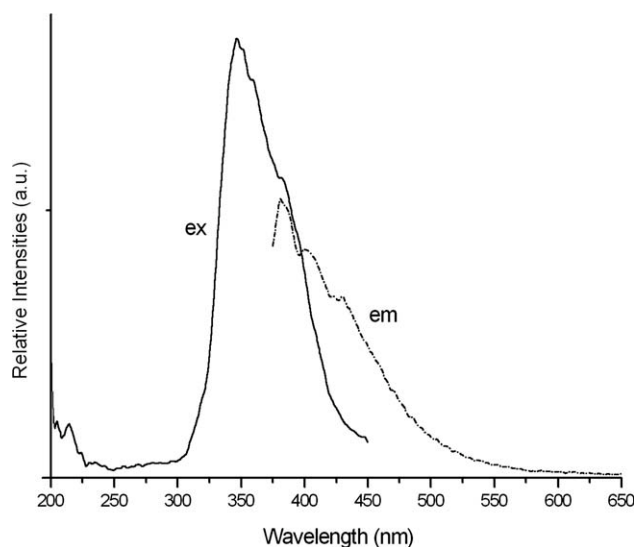
Figure 2 The excitation spectrum and emission spectrum of the 1,10-phenanthroline.

Figure 4 The excitation spectra of the terbium nitrates (a), [Tb(phen)$_3$](NO$_3$)$_3$ (b), and LFPS-T (c).

was observed at 1743cm^{-1} in the curve of the functionalized polysiloxane (c), which also indicated the occurrence of hydrosilylation reaction. From the curve of PMHS (b), the ν(Si-H) vibration was observed at 2160 cm^{-1}. But in the curve of functionalized polysiloxane (c), the ν(Si-H) vibration vanished, which means all Si-H group engaged in hydrosilylation reaction.

Figure 2 is the excitation spectrum and emission spectrum of 1,10-phenanthroline. From the spectra in Figure 2, a excitation band could be found at 346 nm and a broad emission band could be found at 380 nm, which means that 1,10-phenanthroline could absorb ultraviolet light's energy at 346 nm and emit the ultraviolet light at 380 nm.
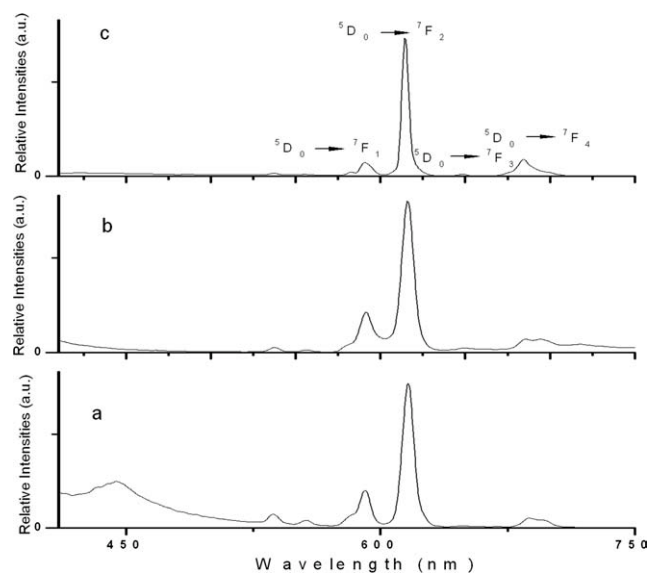

Figure 3 The excitation spectra of the europium nitrates (a), [Eu(phen)$_3$](NO$_3$)$_3$ (b) and LFPS-E (c).

Figure 3 is the excitation spectra of europium nitrates (a), [Eu(phen)$_3$](NO$_3$)$_3$ (b), and LFPS-E (c). They were obtained by monitoring the emission of Eu^{3+} ions at 617 nm. Because of no organic ligand, the excitation spectra of the europium nitrates show poor excitation ability around 350 nm and could only be excited around 390 nm. However, the excitation spectra of [Eu(phen)$_3$](NO$_3$)$_3$ (b) and LFPS-E (c) show many differences with the spectra (a). Compared Figure 3 with Figure 2, a conclusion could be drawn that the 1, 10-phenathroline ligand could absorb the ultraviolet light around 350 nm, emit the ultraviolet light around 380 nm and transfer the energy to lanthanide ion because of the coordination, and then, lanthanide ion show luminescence. The antenna effect took place in these systems.[18] And Figure 4 is the excitation spectra of the terbium nitrates (a), [Tb(phen)$_3$](NO$_3$)$_3$ (b), and LFPS-T (c). Similar circumstances took placed in them. Compared Figure 3 with Figure 4, it is found that the LFPS could enlarge the absorbance of ultraviolet light because of the ligand in ternary lanthanide complexes.
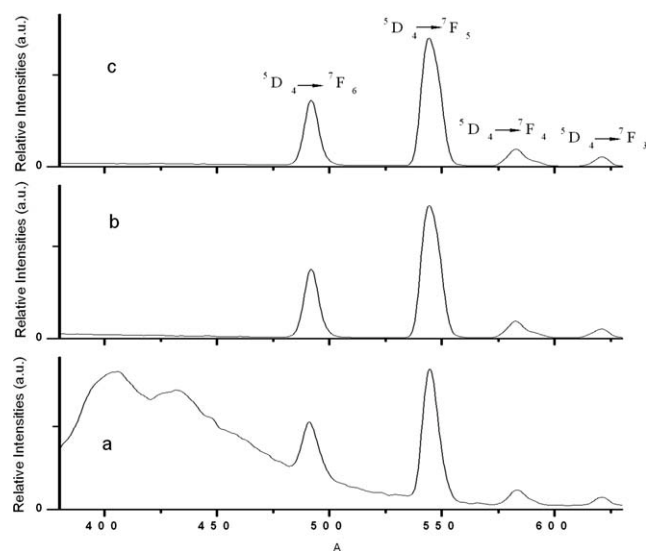
The emission spectra of europium nitrates (a), [Eu(phen)$_3$](NO$_3$)$_3$ (b), and LFPS-E (c) are shown in Figure 5. Narrow-width red luminescence was observed in the spectra of them. The emission bands of the materials were related to the transition from the higher energy level of Eu^{3+} to the different lower energy levels and were assigned to the $^5D_0 \rightarrow {}^7F_1$ (590 nm), $^5D_0 \rightarrow {}^7F_2$ (616 nm), $^5D_0 \rightarrow {}^7F_3$ (652 nm), and $^5D_0 \rightarrow {}^7F_4$ (689 nm) transitions, respectively. A prominent feature that may be noted in these spectra is the high intensity ratios of $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$. The intensity (the integration of the luminescent band) ratio of the $^5D_0 \rightarrow {}^7F_2$ transition to $^5D_0 \rightarrow {}^7F_1$

Figure 5 The emission spectra of the europium nitrates (a), $[Eu(phen)_3](NO_3)_3$ (b), and LFPS-E (c).

Figure 6 The emission spectra of the terbium nitrates (a), $[Tb(phen)_3](NO_3)_3$ (b) and LFPS-T (c).

transition has been widely used as an indicator of Eu^{3+} site symmetry.[25] When the interactions of the lanthanide complex with its local chemical environment are stronger, the complex becomes more nonsymmetrical and the intensity of the electric-dipolar transitions becomes more intense. The detailed data are listed in Table I. The spectra of europium nitrates (a) and $[Eu(phen)_3](NO_3)_3$ (b) show similar intensity ratios because they have similar coordination situation of Eu^{3+}. But the spectrum of LFPS-E (c) has the largest intensity ratio because the carbonyl group participated in the coordination and disturbed the perfect coordination of 1,10-phenanthroline. As a result, $^5D_0 \rightarrow ^7F_1$ transition (magnetic-dipolar transitions) decreased and $^5D_0 \rightarrow ^7F_2$ transition (electric-dipolar transitions) increased. So the intensity ratio increased.

The emission spectra of terbium nitrates (a), $[Tb(phen)_3](NO_3)_3$ (b), and LFPS-T (c) are shown in Figure 6. Narrow-width green luminescence was observed in their emission spectra when the materials were excited at 345 nm. The emission bands of the materials were related to the transition from the triplet state energy level of Tb^{3+} to the different single state levels and were assigned to the $^5D_4 \rightarrow ^7F_6$ (487 nm), $^5D_4 \rightarrow ^7F_5$ (545 nm), $^5D_4 \rightarrow ^7F_4$ (581 nm), and

$^5D_4 \rightarrow ^7F_3$ (621 nm) transitions respectively. And from Figures 5 and 6, it could be concluded that the LFPS could intensify the luminescence of the lanthanide ions.

CONCLUSIONS

In summary, a new kind of EFPS was prepared via hydrosilylation reaction in this article. Green and red luminescence was observed when the functionalized polysiloxane was submitted to complex with 1, 10-phenanthroline and lanthanide ions. It is found that the LFPS could enlarge the absorbance of ultraviolet light because of the ligand in ternary lanthanide complexes. Then it could be concluded that the LFPS could intensify the luminescence of the lanthanide ions. So the method used in this article is a convenient procedure that could be used to synthesize luminescent polysiloxane materials with different loading of various functional groups.

TABLE I
The Luminesence Properties of Lanthanide Nitrates, Lanthanide Complex and LFPS-E

	$^5D_0 \rightarrow ^7F_1$	$^5D_0 \rightarrow ^7F_2$	Relative intensities/a.u.
Europium nitrates	591	616	3.8
$[Eu(phen)_3](NO_3)_3$	591	616	3.0
LFPS-E	591	614	10.5

References

1. El-Nahhal, I. M.; El-Ashgar, N. M. J Organometa Chem 2007, 692, 2861.
2. Hou, A. Q.; Yu, J. B.; Shi, Y. Q. Euro Polym J 2008, 44, 1696.
3. Mazurek, M.; Kinning, D. J.; Kinoshita, T. J Appl Polym Sci 2001, 80, 159.
4. Park, H. S.; Yang, I. M.; Wu, J. P.; Kim, M. S.; Hahm, H. S.; Kim, S. K.; Rhee, H. W. J Appl Polym Sci 2001, 81, 1614.
5. Yahaya, G. O.; Brisdon, B. J.; Maxwell, M.; England, R. J Appl Polym Sci, 2001, 82, 808.
6. Zhou, C. J.; Guan, R. F.; Feng, S. Y. Euro Poly J 2004, 40, 165.
7. Hua, J.; Li, Z.; Qin, J.; Li, S.; Ye, C.; Lu, Z. React Funct Polym 2007, 67, 25.
8. Xie, K.; Hou, A.; Zhang, Y.; J Appl Polym Sci 2006, 100, 720.
9. Xie, K.; Yu, J.; Jiang, D. J Appl Polym Sci 2007, 106, 1256.
10. Xie, K.; Hou, A.; Shi, Y. J Appl Polym Sci 208, 108, 1778.

11. Blass, G.; Grabmaier, B.C. Luminescent Materials; Springer: Berlin, 1994.
12. Maas, H.; Currao, A.; Calzaferri, G. Angew Chem Int Ed Engl 2002, 41, 2495.
13. Klonkowski, A. M.; Lis, S.; Pietraszkiewicz, M.; Hnatejko, Z.; Czarnobaj, K.; Elbanowski, M. Chem Mater 2003, 15, 656.
14. Kuriki, K.; Koike, Y.; Okamoto, Y. Chem Rev 2002, 102, 2347.
15. Bender, J. L.; Corbin, P. S.; Fraser, C. L.; Metcalf, D. H.; Richardson, F. S.; Thomas, E. L.; Urbas, A. M. J Am Chem Soc 2002, 124, 8526.
16. Hasegawa, Y.; Yamamuro, M.; Wada, Y.; Kanehisa, N.; Kai, Y.; Yanagida, S. J Phys Chem A 2003, 107, 1697.
17. Pei, J.; Liu, X. L.; Yu, W. L.; Lai, Y. H.; Niu, Y. H.; Cao, Y.; Macromolecules 2002, 35, 7274.
18. Crosby, G.; Whan, R. E.; Alire, R. J. Chem Phys 1961, 34, 743.
19. Yahaya, G. O.; Brisdon, B. J.; Maxwell, M.; England, R. J Appl Polym Sci 2001, 82, 808.
20. Liu, L.; Lu, H. F.; Wang, H.; Bei, Y. L.; Feng, S. Y. Appl Organometal Chem 2009, 23, 429.
21. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R., Eds. Purification of Laboratory Chemicals; Pergamon Press: Oxford, 1980.
22. Belfield, K. D.; Lin, X. Z. J Polym Sci A Polym Chem 1991, 29, 1073.
23. Yu, J. M.; Teyssie, D.; S. Boileau. J Polym Sci A Polym Chem 1993, 31, 2373.
24. Pretsch, E.; Buhlmann, P.; Affolter, C., Eds. Structure Determination of Organic Compounds, 2nd printing; Springer, Berlin, 2003.
25. Wang, Z.; Wang, J.; Zhang, H. J. Mater Chem Phys 2004, 87, 44.