# Synthesis and Characterization of Novel Magnetic Polymer Microspheres with Photoconductivity

**JUNHUA ZHANG,[1] XIAOBIN DING,[1] YUXING PENG,[1] MANG WANG[2]**

[1] Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, 610041, China

[2] Institute of Polymer Science and Materials, Zhejiang University, Hangzhou, 310027, China

**ABSTRACT:** Functional Fe(III)-phthalocyanine with vinyl groups was synthesized, and the structure was confirmed using Fourier transform infrared spectroscopy and elemental analysis, separately. A novel magnetic polymer microsphere with photoconductivity was prepared by copolymerization of styrene and functional Fe(III)-phthalocyanine, which was used as a comonomer, in the presence of $Fe_3O_4$ magnetic fluid. The structure and morphology of magnetic polymer microspheres were determined by infrared analysis, elemental analysis, thermogravimetric analysis, and scanning electron microscopy. The magnetic responsiveness and photoconductivity were studied. The average size of the microspheres was 38.1 $\mu$, with multidistribution. The microsphere has a good magnetic responsiveness and a good photoconductivity at 762.5 nm. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2609–2614, 2002

**Key words:** Fe(III)-phthalocyanine; magnetic polymer microspheres; copolymerization; photoconductivity; magnetic responsiveness; multidistribution

## INTRODUCTION

In recent years, many functional polymer materials, such as latex, magnetic particles, and gel, have been used as diagnosis and detection carriers.[1–4] Among them, magnetic polymer microspheres with functional groups such as hydroxyl and carboxyl groups, as well as nonfunctional ones, have been attracting much attention for their potential as tools in immunological and medical research as well as in therapy. They have been applied to the studies of cell labeling, phagocytosis, site-specific chemotherapy, radioimmunoassay, enzyme immunoassay, affinity chromatography, chiral catalyst support,[5–7] and so forth.

However, most of these materials are only carriers of bioactive molecular (antigen, antibody, etc.)—other properties of these materials, such as photoconductive and electric properties, have not been used sufficiently.

It's well known that phthalocyanine is a cheap and good photoconductive material that has been widely used as a catalyst as well as a dye.[8–10] In this article, microspheres, which combine the advantages of magnetic separation with photoconductive properties, were designed and synthesized, and these microspheres could be considered for uses, including as a new diagnosis or detection reagent according to its photoconductive signal.
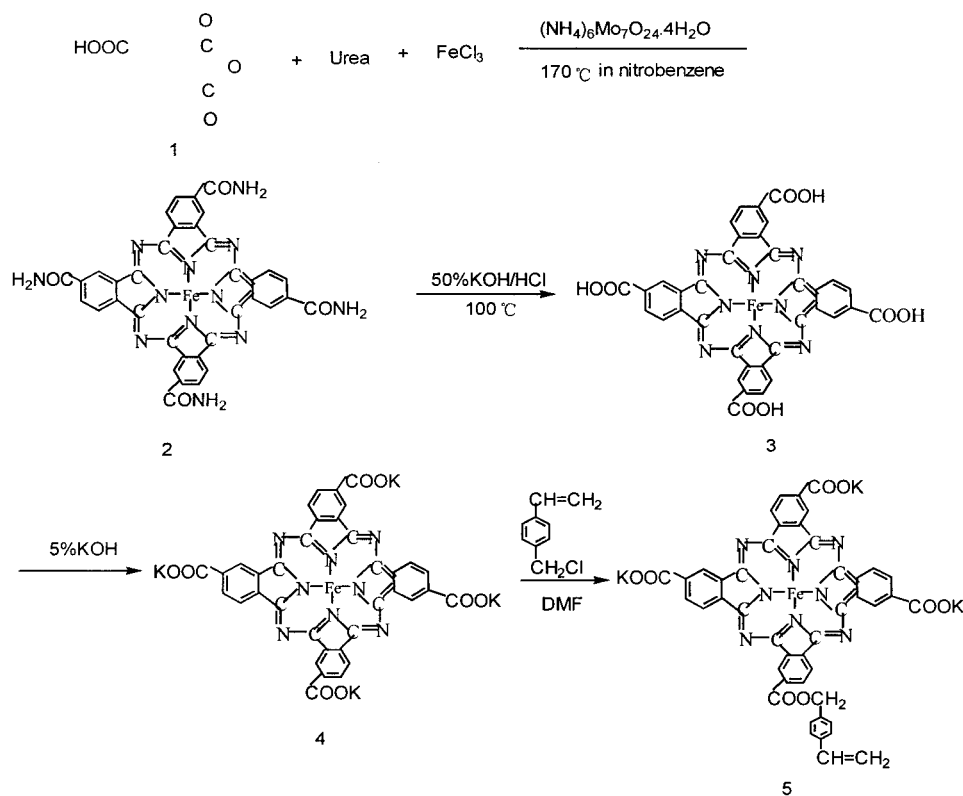
## EXPERIMENTAL

### Materials and Equipment

$FeCl_3$ (analytical reagent grade [AR]), urea (AR), trimellitic anhydride (AR), styrene (St, AR), and other reagents were commercially available. St was

**Scheme 1** The preparation of reactive Fe-phthalocyanine.

washed with 5% NaOH several times to remove the inhibitor and then distilled under reduced pressure. Other reagents were used without further purification. Water was double distilled.

Infrared (IR) spectra of the samples in KBr pellets were recorded on a Nicolet 200SXV Fourier transform infrared (FTIR) spectrometer (USA). Element analyses (C, N) were determined on a EA1108-Elemental Analyzer (Italy); Fe was determined on a ICP-9000(N+M) plasma spectrometer (J-A Co., USA). Morphology was determined with a scanning electron microscope (AM-RAY-1000, China). Thermal gravitation was performed on a Perkin-Elmer TGA7 (USA) under $N_2$, and the raising temperature rate was 10°C/min. The hydrodynamic size in water was tested with a Laser Diffraction Particle Size Analyzer (SHI-MADZU SALD 2001, Japan). Photoconductive properties were performed on a GDT-I model photoconductivity measuring device.
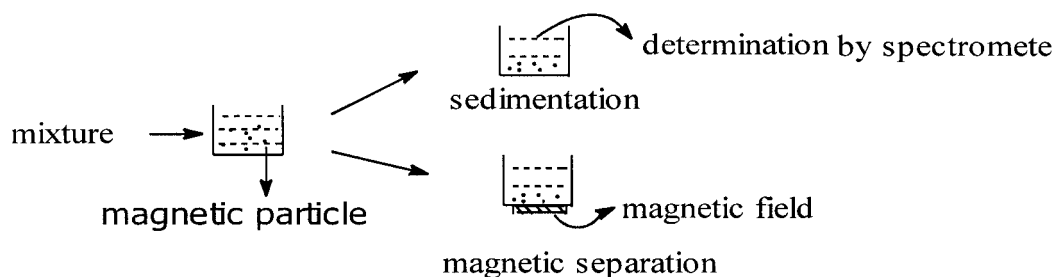
## Preparation of Reactive Fe(III)-Phthalocyanine

The functional Fe(III)-phthalocyanine was synthesized by the process shown in Scheme 1. First, 10.0 g (0.05 mol) of **(1)**, 30.0 g (0.5 mol) of urea, 0.03$M$ FeCl$_3$, 1.0 g (0.001 mol) of ammonium molybdate, and 150 mL of nitrobenzene used as a solvent were mixed in a 250-mL round-bottomed flask equipped with a reflux condenser. The reaction mixture was heated to 170°C for 3 hr, after which a blue solid **(2)** was obtained. It was washed with methanol to remove nitrobenzene and dried for 24 hr at 60°C in vacuum. Second, **(2)** was hydrolyzed to **(3)**. The hydrolysis was carried out by boiling in 50% KOH for 8–10 hr and subsequent neutralization with concentrated HCl, according to the method given by Schutten and Zwart.[9] After purification by washing twice with acetone and ether, the product was dried for 24 hr at 60°C in vacuum. Third, **(3)** was solved in a 0.1 N KOH solution, and the solution precipitated with ethanol. The precipitate was collected with the aid of a centrifuge and washed with ethanol and acetone and dried for 24 hr at 100°C in vacuum; **(4)** was obtained. Finally, **(5)** was synthesized by **(4)** with 4-vinylbenzyl chloride in DMF at 80°C for 24 hr. A black solid was acquired.

## Synthesis of Magnetic Polymer Microspheres

A total of 10.0 g magnetic fluid (according to our previous work,[12] the average diameter is about 50

**Scheme 2** Method for determining the magnetic responsiveness.

nm), 15.0 g styrene, 0.1 g reactive Fe(III)-phthalocyanine, 6.0 g poly(ethylene glycol)(PEG-4000), 0.45 g potassium persulfate (KPS), and $H_2O$/$C_2H_5OH$ were mixed in a 250-mL round-bottomed flask equipped with a reflux condenser. The reaction mixture was kept at 70°C for 10–12 hr under a $N_2$ atmosphere, after which the product was washed with $1M$ HCl solution to remove the unenclosed $Fe_3O_4$ and separated in a magnetic field. The final product was dried for 24 hr at 60°C in vacuum. The microsphere's yield was about 80%.

**Detection of Magnetic Responsiveness**

Our lab established a method to detect magnetic responsiveness (see Scheme 2). First, 1.0 g magnetic microsphere was suspended in 20 mL $H_2O$, then the transmittance of the suspension solution was determined by spectrometer (721) at 580 nm at a certain time under a 0.42-T magnetic field.

**Preparation of Photoreceptor Device and Measurement of Its Photoconductivity**

A double-layered photoreceptor device (P/R) is made by coating the interface layer (IFL), the charge-generation layer (CGL), and the charge-transportation layer (CTL) successively onto an aluminum substrate. The IFL is polyamide. The CTL contains $\alpha$-naphthalic hydrazone (NPH), polycarbonate (PC), and polyvinylcarbazole (PVK) (4 : 4 : 1, by weight). The CGL is formed by 0.1 g magnetic polymer microsphere, 0.025 g polyvinyl butyral (PVB), 10 mL tetrahydrofuran (THF), and 15 g glass beads stirred for 6 hr.

A GDT-I model photoconductivity-measuring device was used under different wave numbers to acquire photoconductive data: charge acceptance ($V_c$), residual potential ($V_r$), dark decay (DD), and the time from the original potential to half value on exposure ($t_{1/2}$). The $t_{1/2}^{-1}$ can indicate photo-
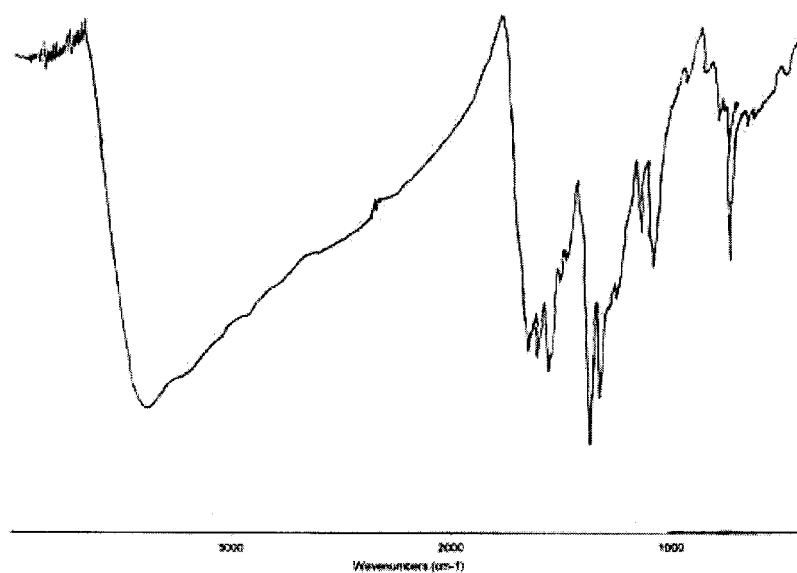


**Figure 1** Infrared spectra of functional FE(III)-phtalocynine.
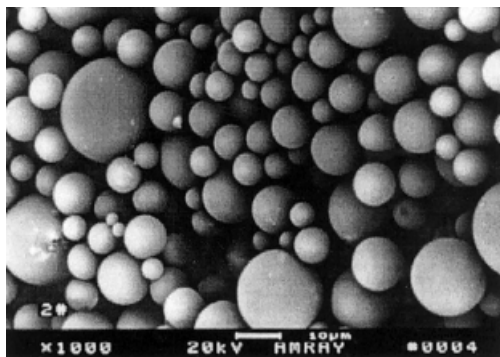
**Figure 2** Scanning electron microscope photograph of magnetic polymer microspheres.

sensitivity: The bigger the $t_{1/2}^{-1}$, the higher the photosensitivity.

## RESULTS AND DISCUSSION

In dispersion polymerization, the mixture solvent must dissolve monomer but precipitate the forming polymer. In our study, functional Fe(III)-phthalocyanine as a copolymer agent is a solid that cannot be dissolved by water/ethanol. In early time, one-hand magnetic particles would adsorb some stabilizer, St, functional Fe(III)-phthalocyanine, and initiator on its surface,; however, functional Fe(III)-phthalocyanine would adsorb some stabilizer, St, and initiator as a center. On heating, the initiator de-

composed and the free radicals reacted with St and functional Fe(III)-phthalocyanine to form $Fe_3O_4$/oligomeric or **(5)/**oligomeric radicals. At the same time, some oligomeric radicals were generated in the solution. At a critical chain length, the oligomers precipitated, aggregated, and adsorbed stabilizer to form stable bigger particle nuclei. Once the particles are formed and stable, they adsorbed monomer at the surface and grew further though polymerization within the monomer-swollen particles until the monomer was consumed.

The structure of the functional Fe(III)-phthalocyanine monomer was determined using FTIR, and result is shown in Figure 1. The absorption band at 1654 cm$^{-1}$ is attributed to carboxyl stretching, and the reason behind the value, which is lower than normal, is the conjugation effect in the molecular. The absorption band at 1612 cm$^{-1}$ is the result of the stretching of the carbon–carbon double bond.

The composition of this monomer was also determined using elemental analyzer. The results are shown as follows: $FeC_{45}H_{15}N_8O_8$ (860) calc. C 62.79%, H 1.74%, Fe 6.51%, N 13.0%; found: C 62.90%, H 1.78%, Fe 6.46%, N 12.61%. Obviously, the levels of N and Fe obtained by experiment quite agree with the values calculated according to the formula.

Figures 2 and 3 show the photograph and particle distribution of magnetic polymer microspheres, respectively.
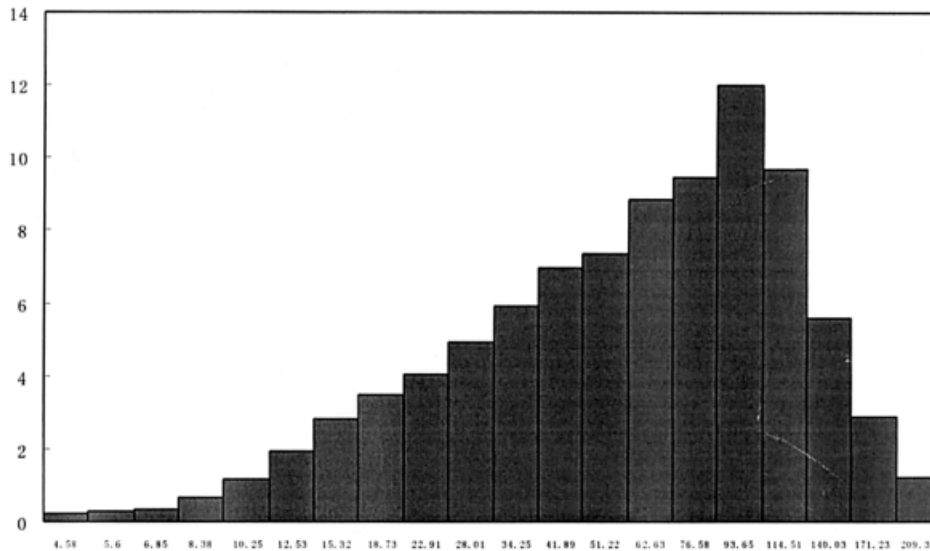


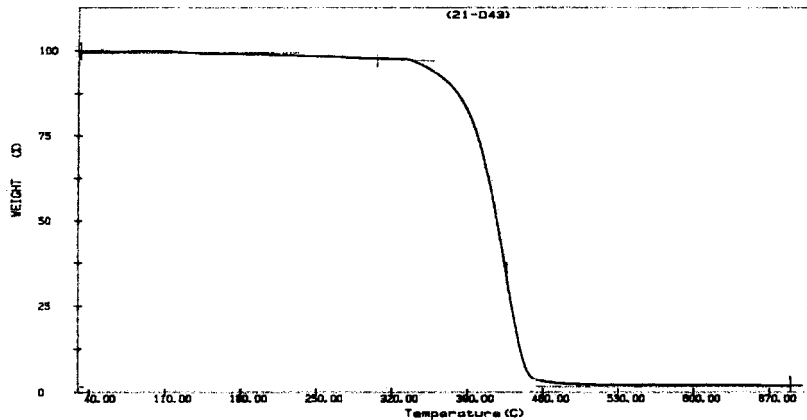**Figure 3** Histogram of magnetic polymer microspheres.

**Figure 4**   Thermal analysis curve of magnetic polymer microspheres.

The results showed that the average size of the microspheres was 38.1 $\mu$m with multidistribution, probably resulting from some earlier formed particles aggregated together, or else they grew faster than other particles formed later. We noticed that more than 80% of the magnetic polymer microspheres range from 10 to 85 $\mu$m, and the microspheres with different average sizes could be synthesized by changing copolymerization conditions.

The microsphere is a core–shell structure. The core is $Fe_3O_4$ magnetic fluid, and the shell is a copolymer of styrene and Fe(III)-phthalocyanine. We studied the composition of the microsphere. Noguchi et al.[5] investigated the magnetite content in magnetic polymer microspheres by thermal analysis (TG). They raised the temperature to 900°C, at which point the organic part of microspheres decomposed and the inorganic component are at rest. In fact, for polystyrene microspheres, there is no further weight loss when the temperature excess 600°C, so it's enough to raise the temperature to 700°C. The result is shown in Figure 4. From the result we can see that the residue weight is about 1.925% at 700°C, attributed to two parts: magnetic fluid ($Fe_3O_4$) and Fe, which is contained in the functional Fe(III)-phthalocyanine.

The content of Fe(III)-phthalocyanine in the microspheres could be calculated from the value of the N element, which was obtained using elemental analyzer. The result showed that the content of N in the microspheres is 0.18%; in other words, the content of Fe(III)-phthalocyanine is about 1.43%. Of course, Fe of Fe(III)-phthalocyanine in a microsphere is also easily calculated—it is 0.092%—so the content of magnetite in microsphere is equal to 1.925% − 0.092%, or 1.833%.

Photoconductivity of magnetic polymer microspheres was measured on a double-layered photoreceptor device (P/R) under different wave numbers. The result are shown in Table I. The exposure is 30 lux. We note that $V_c$ and DD showed an irregular increase and that $t_{1/2}$ showed a decrease with an increasing wave number. Mang et al.[13] investigated the photoconductivity of PVK-co-CuPc(COOH)$_3$. They found that the photoconductivity is better than that of CuPc(COOH)$_4$ for the bigger $\pi$ conjugated between CuPc(COOH)$_3$ and PVK main chain. In our work, the polymer shell is polystyrene, which has no group to conjugate with Fe(III)-phthalocyanine; it acted as an impurity, in fact. In addition, the grafting ratio of Fe(III)-phthalocyanine is not high (1.43%), so the data did not show a regular change with an increasing wave number. However, there is a high charge acceptance ($V_c$ = 824V) and a low residual potential ($V_r$ = 77V) when the wave number is 762.5 nm, although DD (DD = 343 V/s) is large, which indicates that the charge retention is not very good. The time of half discharge $t_{1/2}$ is 0.94, which indicates that the microsphere has good photosensitivity.

**Table I   Photoconductivity of Photoreceptor Device from Magnetic Polymer Microspheres**

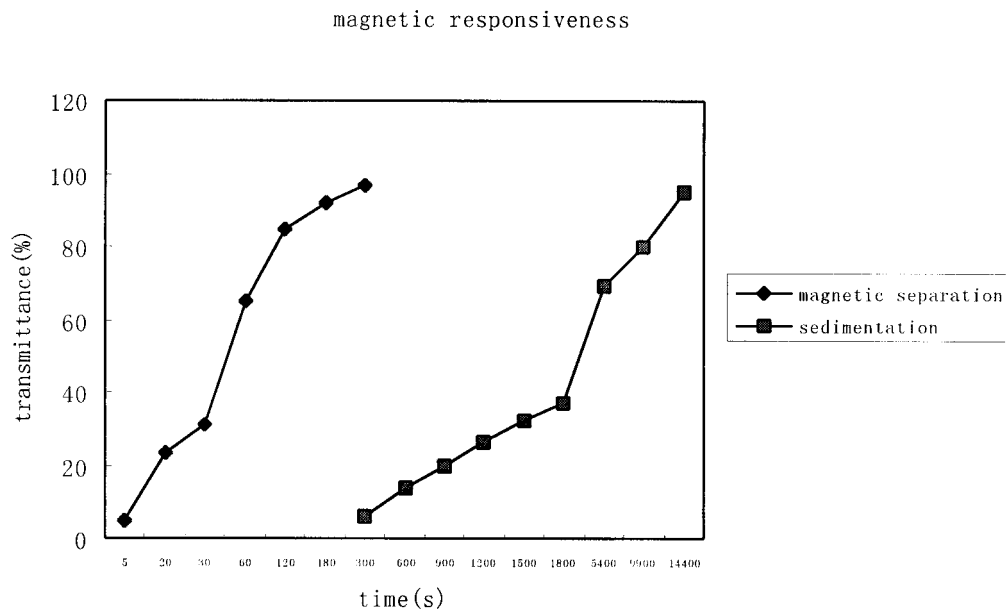| Wavelength (nm) | $V_c$ (v) | $V_r$ (v) | DD (v/s) | $t_{1/2}$ (s) |
|---|---|---|---|---|
| 454 | 679 | 277 | 63 | 1.03 |
| 500 | 578 | 277 | 48 | 0.72 |
| 570 | 652 | 281 | 58 | 0.93 |
| 605 | 640 | 52 | 285 | 1.08 |
| 678.7 | 610 | 75 | 308 | 1.09 |
| 703 | 749 | 69 | 218 | 0.89 |
| 762.5 | 824 | 77 | 343 | 0.94 |

magnetic responsiveness



**Figure 5** Magnetic responsiveness of magnetic polymer microspheres.

Magnetic responsiveness is an important property of magnetic particles. Using this property, we can realize fast separation and purification, convey target drugs at the proper site in the human body,[14-15] and so forth. Figure 5 is the magnetic responsiveness results of magnetic polymer microsphere under a magnetic field and natural sedimentation. It was found that it cost only about 5 min for the supernatant transmittance to reach 95%; in contrast, it cost about 4 hr in natural sedimentation. So the magnetic polymer microsphere has good magnetic responsiveness, which will be helpful in shortening the time consumption of separation and purification and even to locate the microsphere at an expected site in the human body under a magnetic guide.

## CONCLUSION

A functional Fe(III)-phthalocyanine monomer and a novel magnetic polymer microsphere combining magnetic and photoconductive properties were synthesized. The average size was 38.1 $\mu$m. Fe(III)-phthalocyanine content in the microsphere is 1.43%; magnetite content is 1.833%.

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