

A novel paramagnetic polymeric sensor material sensitive to organic molecules

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Utilizing the Diels-Alder reaction between cyclopentadiene groups attached on the linear polystyrene in the presence of nitroxide free radicals, a novel cross-linked network containing nitroxide free radicals is prepared. The signals of the electron spin resonance (ESR) from the resultant paramagnetic polymeric material contacting with organic molecules are different from uncontacting with organic molecules obviously. And the response from the organic molecules to organic molecules free or vice versa was reversible. Therefore, the resultant material is a novel paramagnetic polymeric sensor material sensitive to organic molecules and can be used for detecting the presence of organic molecules or the absence of organic molecules.

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1. Introduction

Over the past two decades, the development and applications of sensors have grown rapidly. Among all sensors, polymer-based sensors have received the most attention because of the importance in various scientific research and practical applications [1–4]. Magnetic polymeric materials play an important role in polymer-based sensor materials. In the work described in this paper, we utilized the Diels-Alder reaction between the cyclopentadiene groups attached on the linear polystyrene to form cross-linked network structure [5] and encapsulated nitroxide free radicals in the network without chemical bonding to the polymer during Diels-Alder reaction. By this method, a novel paramagnetic polymeric material was prepared. The possibility of resultant materials used for detecting the presence of organic molecules or the absence of organic molecules was discussed.

2. Experimental section

2.1. Materials

All the operations were carried out under dry argon atmosphere using the standard Schlenk techniques. Hexamethylphosphoramide (HMPA) and 4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy (4-Oxo-TEMPO) free radicals were purchased from Aldrich. 1-Nitropropane and dicyclopentadiene were purchased from ACROS. Chloromethyl methyl ether was purchased from TCI. These agents were used without further purification.

Tetrahydrofuran (THF) was distilled from Na/K alloy under argon atmosphere. Cyclopentadiene was obtained by cracking dicyclopentadiene under argon atmosphere and styrene was distilled prior to use. Cyclopentadienylsodium (CpNa) was synthesized according to the literature [6].

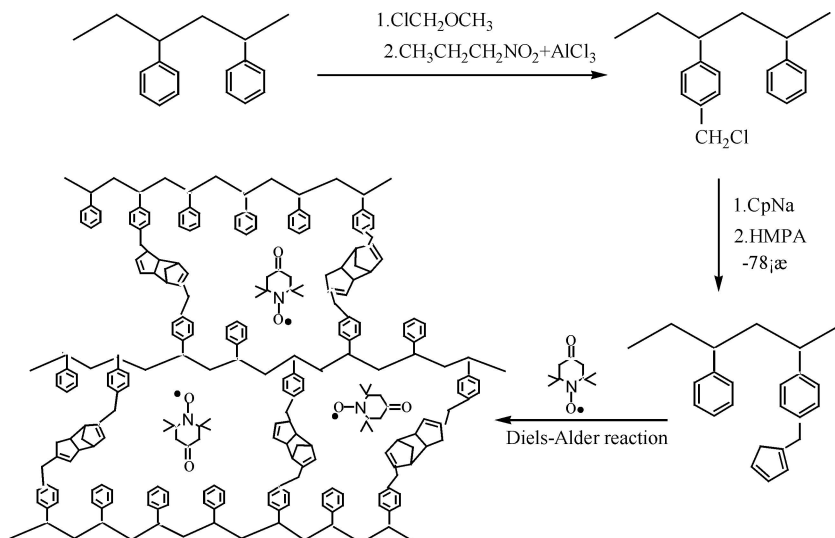
2.2. The preparation of linear polystyrene

The linear polystyrene was prepared by suspension polymerization. The typical reaction is as follow: 2 g of polyvinyl alcohol was dissolved in $500 \times 10^{-6} \text{ m}^3$ of deionized water. Subsequently, 100 g of styrene and 3 g of benzoyl peroxide were added. The mixed solution was warmed to 80°C and stirred for 3 h. The product was dried under vacuum overnight.

2.3. The synthesis of chloromethylated polystyrene

1.5 g of the resultant polystyrene was dissolved in $150 \times 10^{-6} \text{ m}^3$ of CCl_4 . Subsequently $2 \times 10^{-6} \text{ m}^3$ of chloromethylmethylether and a catalyst solution (containing 1 g of anhydrous AlCl_3 , $7 \times 10^{-6} \text{ m}^3$ of 1-nitropropane, $57 \times 10^{-6} \text{ m}^3$ of CCl_4) were added in order. The reaction was performed for 3 h at room temperature and quenched using 10 mL of glacial acetic acid. The resultant product was precipitated using anhydrous methanol, then washed and filtrated. Finally the product was dried under vacuum overnight.

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Scheme 1 The preparation scheme of novel paramagnetic polymeric sensor materials.

2.4. The synthesis of cyclopentadienylated polystyrene

0.36 g (0.54×10^{-3} mol of chloromethyl groups) of chloromethylated polystyrene was dissolved in 30×10^{-6} m³ of THF. Subsequently, the above-mentioned solution and 7×10^{-6} m³ of HMPA were added via syringe into the 30×10^{-6} m³ of CpNa/THF solution (0.75 mol/ 10^{-6} m³) at -78°C in order. The mixture was gradually warmed to 0°C and reacted for 3.5 h at 0°C . The reaction was quenched using 8×10^{-6} m³ of the saturated solution of NH_4Cl . Then, the resultant product was precipitated using anhydrous methanol, washed and filtered at 0°C . Finally, the resultant product was dried under vacuum for 24 h at 0°C .

2.5. The preparation of paramagnetic polymeric material

Two samples containing different contents of free radicals were prepared. Sample 1: 2.4 mg of 4-Oxo-TEMPO and 35 mg of cyclopentadienylated polystyrene were dissolved in 10×10^{-6} m³ of THF. Then, the solvent was removed under vacuum. The residual solid complex performed Diels-Alder cross-linked reaction for 8 days at room temperature. During the Diels-Alder reaction of cyclopentadiene groups, the radicals were encapsulated in the cross-linked network. Finally the sample was washed by methanol to remove the radicals absorbed on the surface of polymer. Sample 2: 4.8 mg of 4-Oxo-TEMPO and 35 mg of cyclopentadienylated polystyrene were dissolved in 10×10^{-6} m³ of THF. Subsequently, the Sample 2 was treated by the above-mentioned method.

2.6. Characterization

The molecular weight and molecular weight polydispersity of the linear polystyrene were determined by GPC (Waters 150 C) at 20°C using THF as solvent. The content of chloromethyl groups attached to the polystyrene was determined by ^1H NMR (Bruker AVANCE DMX500) spectroscopy by comparing the

integral of the methylene signal at $\delta = 4.49$ ppm with that of the aromatic region. The contents of radicals leached off to methanol were determined by liquid chromatography. The difference between the gross amount of radicals added and amount of radicals leached off to methanol was the content of radicals encapsulated in cross-linked polystyrene network. ESR spectra were recorded by JEOL JES-FEIXG ESR. The value of g factor was determined by comparison to that of an Mn^{2+} standard substance according to following equation:

$$g = \frac{1 - \frac{\Delta X_4}{\Delta X_3}}{1 - \frac{g_4}{g_3} \times \frac{\Delta X_4}{\Delta X_3}} \times g_4$$

where g_3 and g_4 are the g values of the third and fourth peak of Mn^{2+} , respectively. ΔX_4 and ΔX_3 are the distance between g_3 , g_4 and the peak whose g value needs to be calculated.

3. Results and discussion

The preparation procedure of the novel paramagnetic polymeric sensor materials was as shown in Scheme 1. The linear polystyrene was chloromethylated and then the chloromethylated polystyrene reacted with CpNa

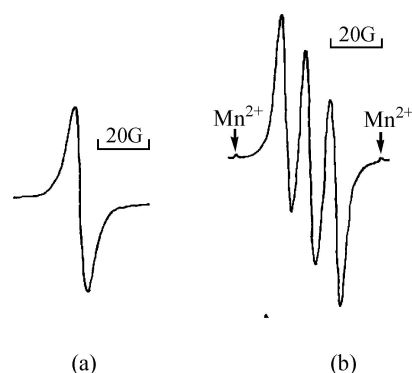
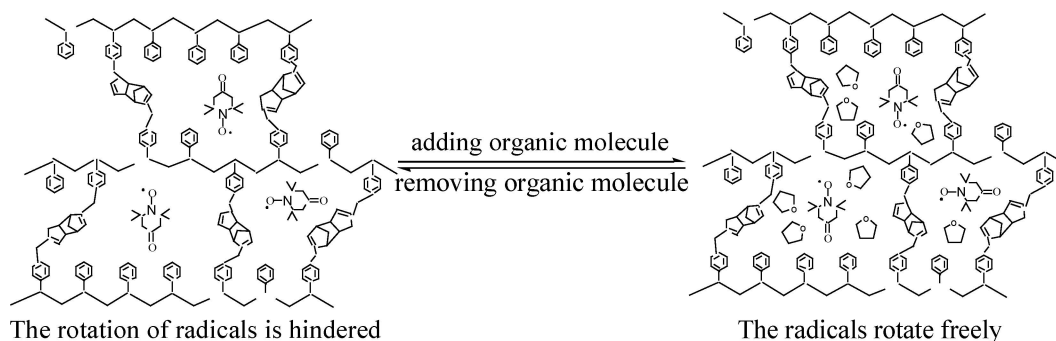


Figure 1 ESR spectra of pure radicals at 20°C . (a) Solid radicals sample, $g = 2.0058$. (b) radicals dissolved in THF, $g = 2.0057$.



Scheme 2 The reversible change model between paramagnetic polymeric sensor material containing organic molecules and not containing organic molecules.

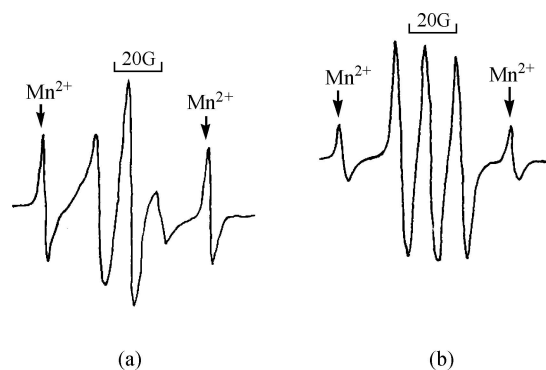


Figure 2 ESR spectra of resultant paramagnetic polymeric material at 20°C. (a) Sample 1, $g = 2.0057$, (b) Sample 1 containing organic molecule THF, $g = 2.0057$.

to form cyclopentadienylated polystyrene. The different contents of the radicals (4-Oxo-TEMPO) and cyclopentadienylated polystyrene were dissolved in THF. Subsequently, the THF was removed under vacuum, then the residual solid performed Diels-Alder reaction at room temperature to form the cross-linked network containing the radicals.

The molecular weight of polystyrene, $M_w = 34600$, and the polydispersity, $M_w/M_n = 1.88$, were determined by GPC analysis. The content (16.85%) of chloromethyl groups of the chloromethylated polystyrene was determined by ^1H NMR spectroscopy by comparing the integral of the methylene signal at $\delta = 4.49$ ppm with the integral of the aromatic region. An excessive amount of CpNa was used to react with chloromethylated polystyrene in order to transform completely the chloromethyl groups to cyclopentadienide groups. ^1H NMR spectroscopy showed the conversion of the chloromethyl groups was complete as indicated by a highfield shift of the methylene signals from $\delta = 4.49$ ppm before reaction to $\delta = 3.60$ ppm after traction. The contents of radicals in Samples 1 and 2 were 1.47 mg, 1.98 mg, respectively.

The ESR spectrum of pure solid radicals without hyperfine splitting is shown in Fig. 1a. After dissolving radicals in THF, a typical ESR spectrum characterizing the rapid rotation of radicals in solution was observed as shown in Fig. 1b. Owing to restriction of the rapid rotation of radicals, the anisotropic ESR spectra of the samples containing different contents of radicals in the interior of the cross-linked polymer in the ab-

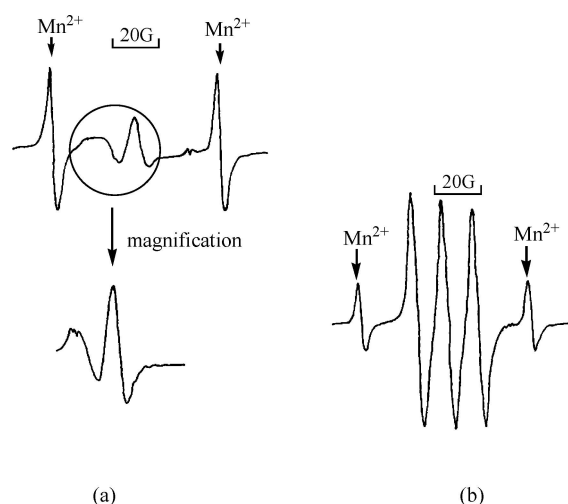


Figure 3 ESR spectra of resultant paramagnetic polymeric material at 20°C. (a) Sample 2, $g = 2.0058$. (b) Sample 2 containing organic molecule THF, $g = 2.0057$.

sence of organic molecules were observed as shown in Fig. 2a, > 3a. The pattern of ESR signals indicated that the microenvironments of encapsulated nitroxide radicals were different from the microenvironments containing organic molecules. Comparing Fig. 2a with Fig. 3a, it is found that there were stronger hyperfine splitting patterns in Fig. 2a. The reason is that in Sample 2 there were more radicals and the spin-spin interaction of radicals was stronger than that of Sample 1.

After the sample was contacted with organic molecule THF, the spectra revealed hyperfine splitting and isotropic characters as shown in Figs. 2b and 3b. The phenomena indicated that organic molecule THF penetrated the polystyrene cross-linked network and swelled the network, and radicals encapsulated in the network rotated freely. After the sample contacting organic molecules THF was vacuumed and the organic molecules was removed, the rotation of the radicals were hindered and the ESR signals returned from signal shown in Fig. 2a to b or from Fig. 3a to b again. The reversible changes of ESR signals arise from the reversible change of microenvironment in which the paramagnetic radicals exists. In other words, the resultant polystyrene network containing radicals is a useful novel paramagnetic polymeric sensor material sensitive to organic molecules. The reversible change model can be shown in Scheme 2.

4. Conclusions

A convenient method of introducing free radicals into a polymer was described and a novel paramagnetic polymeric sensor magnetic material was prepared. Compared with other methods for obtaining polymeric materials [7–12], this method was convenient and versatile. In addition, the novel paramagnetic polymeric material was sensitive to organic molecules. The behaviors of the paramagnetic polymeric material in different environments were studied in detail by electron spin resonance (ESR). The result showed the paramagnetic polymeric material encapsulating nitroxide radicals were sensitive to organic molecules and was a useful and novel paramagnetic polymer sensor material.

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