

Pilot study of magnetic pitch resin

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1. Introduction

Magnetism is one of mystery properties for functional organic compounds. As the development of electronic industry has been growing rapidly nowadays, the need for lightweight organic magnetic material is considerably increasing. So far, there are two main types of organic magnetic materials being researched in current researching area. One is the soluble complex compound, which is able to cause shifting electric charges in a solvent. Another one is polymer. For instance, the Condensed Polynuclear Aromatic resin (pitch resin) is one of such kind polymers. Previous studies showed that there were many defects in these kinds of organic magnets, the soluble complex compound only exhibited magnetism at extreme low temperature (below 4K) and the yield of polymer organic magnet was very low and its stability not good [1].

It is well known that the organic compounds usually are diamagnets. But once the hydrogen atoms escaped from an organic group, a radical would be formed. When the amount of radicals was increased, the organic groups would display normal magnetic properties. If all the radicals were oriented in an order of polarity, basic weak magnetic units were constructed. These basic weak magnet units formed a strong organic magnet once they were oriented in a further regular order [2]. In 1986, Ovchinnikov obtained the first strong organic magnet, which was derived from the stabilized diacetylene radical substitutes [3]. Since the reaction was photo initiated solid phase polymerization, only 0.1% of the product was found to be ferromagnetic. Japanese and American investigators Iwamura and Torrance claimed their findings of organic magnets respectively years later [2,3]. But the research results were regarded not convincing because of lacking sound evidences of characterization [4]. It was found in Ota's study that the most special characteristic of pitch resin molecular structure was its contained methine substructure[5]. In other words, the aromatic nuclear was connected to each other by methines. Owing to the existence of π electrons in aromatic nucleus as well as the easiness of forming a radical ,because hydrogens in the methine substructure are very ready to escape, the pitch resin exhibits a specific magnetic behavior. If the organic macromolecular magnet could be obtained, it would be surely to become a novel functional material of low density and it would possess a very high application value in future. In this study, Pyrene is used as a starting material and Benzaldehyde as a cross-link agent, Para-toluene sulfonic acid as a catalyst and a pitch resin is synthesized. Its structural characteristics and its magnetic properties are primarily investigated.

2. Experimental

2.1 Raw material

Pyrene (Py, 99% purity) was purchased from Aldrich chemical co. and Benzaldehyde (BA, reagent grade) from Shenyang chemical reagent factory. Para-toluene sulfonic acid (PTS, chemical grade) was obtained from Shanghai chemical reagent company.

2.2 Synthesis of B- stage pitch resin

The synthesis of B –stage pitch resin is carried out under the conditions that the mixing ratio of PY/Ba is 1.5, the percentage of PTS in total starting material is 5%, reaction temperature is 160°C, reaction time is 1.5hr.

The molecular weight of pitch resin, measured via VPO method, is 1700. Pitch resin was firstly dissolved in toluene, and then it precipitated by adding alcohol to the solution. The deposits were obtained through filtration. The brown colored solid powder was left after vacuum drying. The powder was purified by alcohol extraction again. Finally, purified B-stage pitch resin (solid powder) was obtained.

2.3 Carbonization of B-stage pitch resin

A specific amount of B stage pitch resin was placed into a tubular carbonizing furnace. The specimen was heated up to 500 °C, 600 °C, 700 °C respectively in a N₂ atmosphere with a raising temperature rate of 1~2°C/min and the temperature was maintained for 2 hours at each run. The bright black carbonaceous product was obtained at last.

2.4 Spectroscopy analysis

An American FTS-15CFT-IR Digital spectrometer was employed to record the IR spectra with a resolution of 4cm⁻¹. NMR spectroscopy was carried out on an American Varian Unity 200MHz superconductor nuclear magnetic resonance spectrometer. The KBr tablet method was used for sample preprocessing, using CDCl₃ as solvent, TMS as internal standard. ¹H-NMR Scanning frequency is at 80MHz, scanning range 2000Hz. ¹³C-NMR scanning frequency is at 20MHz, scanning range is at 5000Hz, acetylacetone chromate Cr(AcAc)₃ used as relaxation reagent, reversal gating technique was employed to uncouple the sample. Both resolutions of ¹H-NMR and ¹³C-NMR were less than 0.2Hz. ESR was performed on a JES-FELXG electron-Spin resonance spectrometer and operational parameters were scanning field range 3400 ± 250G, power 1mW, internal standard manganese spectral line, adjusting scope 2G, frequency 100KHz, scanning time 8min/360mm, response time 0.03S.

3 Results and Discussion

3.1 Structural Characterization of Py/BA pitch resin

Contents of H%, O% in B stage pitch resin was very high (Table 1). It implied that the most of the condensed polynuclear aromatic molecules remained in the early stage of configuration and a large amount of not fully reacted components of original materials was still contained in pitch resin. Therefore, the preprocessing of sample was of very important significance.

Table 1 Basic properties of B-stage pitch resin

Softening point °C	Elemental composition				Molecular weight	Solubility
	C %	H %	O %	H/C		
70.12	88.36	8.32	3.32	1.13	1700	Soluble in toluene, benzene, tetrahydrofuran, CH ₂ Cl ₂ , etc.

Standard chemical shift values of ¹H-NMR spectrum for Py and BA are displayed as following[6] :



Figure 1. Standard chemical shift values of ¹H-NMR spectrum for Py and Ba

Py ring is a planar symmetrical molecule. Once polymerization reaction occurred, the hydrogen attached to Py ring was replaced. Then, the symmetry of hydrogen on Py ring is destroyed. The uneven distribution of electronic cloud caused the mutual disturbance between different spinning hydrogen nucleus. Therefore a series of relatively complicated peaks could be detected via NMR.

As shown in figure 2, peaks A whose δ value of is 7.99~8.20, is belonged to the chemical shifts of the hydrogen on Py ring in pitch resin molecule. The peaks B and C whose δ value is 7.20~7.60, is corresponded to the chemical shifts of hydrogen on the benzene ring in pitch resin molecule. In Figure 2, that no peak whose chemical shift is further than 9.00 indicates that unreacted aldehyde group components were totally removed from the refined pitch resin. With the evacuation of the effect of aldehyde group to the hydrogen on benzene ring, the chemical shifts were moved toward upfield, which were completely departed from the position of the peak of hydrogen attached to Py ring.

In the standard spectrum, the chemical shift for the methyl hydrogen in tri-aryl methane type structure is $\delta = 5.50$. It can be deduced from figure 2 that D peak ($\delta = 6.66$) apparently is the chemical shift of tri-aryl methyl hydrogen whose aromaticity is much higher. Generally, it is regarded that the condensed aromatics in the refined pitch resin possesses a stronger deshielding action, therefore the chemical shifts transited toward down field.

By means of Integration of each peak area, it can determined that hydrogen of Py ring : Hydrogen of Benzene ring : hydrogen of tri-aryl methyl is about 8 : 5 : 1. It can be concluded that double displacement reaction occurred to Py ring, but a single displacement reaction occurred to benzyl ring.

In Figure 3, peak A and peak B are corresponded respectively to the carbon on benzyl ring and the carbon on py ring connected with methane. A set of peaks C is corresponding to the aromatic carbons on benzene ring and Py ring. Owing to the substitution of methane, the density of electronic cloud on pitch resin molecule was declined. Consequently, its chemical shifts moved toward downfield a bitter than that of mono py ring and benzene ring. Peak D ($\delta = 50.31$) was determined to be caused by the carbon of tri-aryl group methyl. The chemical shifts for aldehyde carbons, more than 180, did not appear (figure 3).

From the infrared spectra (figure 4), the peaks caused by the stretching vibration of the hydroxy in formaldehyde disappeared at 1700cm^{-1} . But peaks caused by the stretching vibration of C-H in tri-aryl methyl appeared at 3040cm^{-1} . All these phenomena proved that the B-stage pitch resin derived from Py/Ba possessed the tri-aryl methane structure.

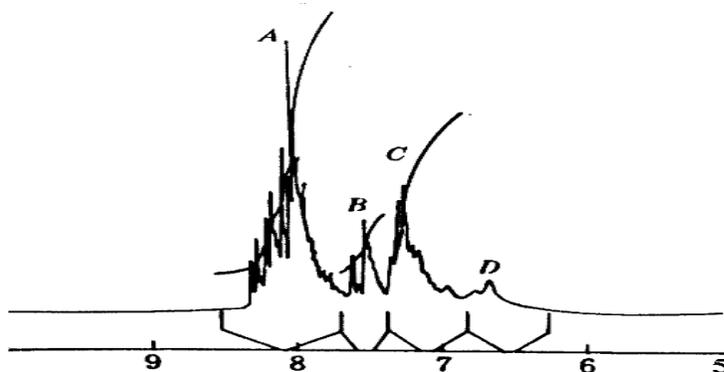


Figure 2. $^1\text{H-NMR}$ spectrum of refined Py/Ba pitch resin

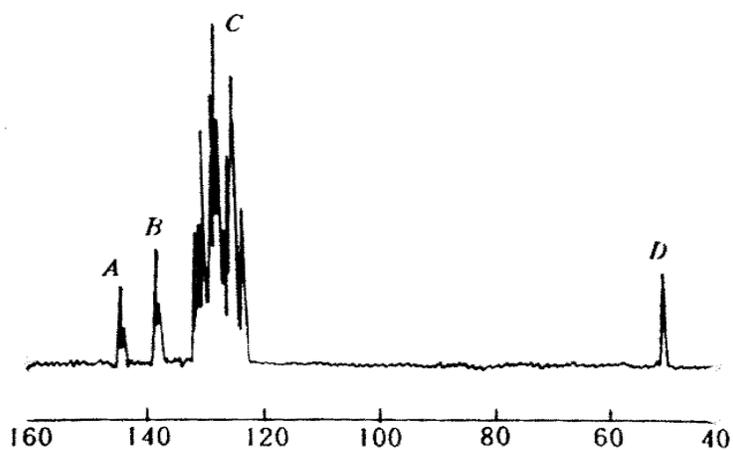


Figure 3. $^{13}\text{C-NMR}$ spectrum of refined Py/Ba pitch resin

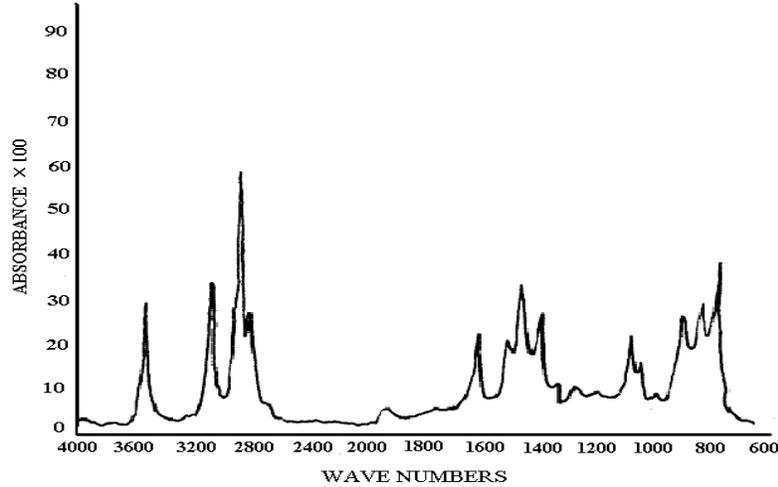


Figure 4. IR spectrum of refined Py/Ba pitch resin

According to the analysis above, the route of synthesis of pitch resin could be deduced. With the assistance of the catalyst PTS, BA molecules were converted into free radicals at first, then the radicals attacked the Py rings and the electrophilic displacement reaction occurred at the same time. Consequently the Py rings were connected to each other. The reaction procedure is shown as following :

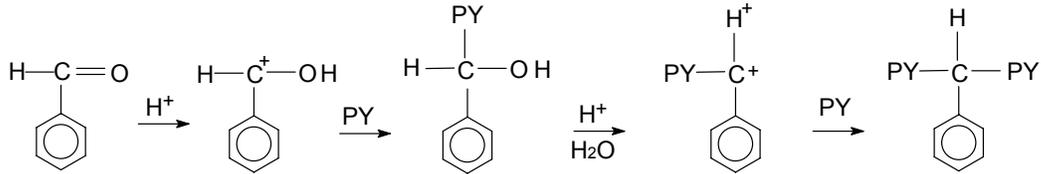


Figure 5. Proposed route of synthesizing pitch resin from pitch resin

3.2 ESR analysis for the carbonized pitch resin

B-stage pitch resin was heat-treated at the temperature of 500°C, 600°C, 700°C under an inert gas shielding respectively (dehydrogenate heat-treatment). The test results by ESR were listed in Table 2.

Table 2 ESR test results at different temperatures

Carbonizing temperature °C	Concentration of free radical /Spin .g ⁻¹	g- value	Peak width/10 ⁻⁴ Tesla
Un-carbonized	4.94 × 10 ¹⁴	2.01	7.58
500	2.14 × 10 ²²	2.02	12.56
600	5.67 × 10 ²⁰	2.01	6.72
700	7.35 × 10 ¹⁸	2.01	8.19

It can be seen that a high-spin substance can be obtained from B stage pitch resin after 500°C carbonizing treatment (Table 2). This is because the chemical bond of (C-H) on

methenyl was ruptured with the effect of heat treatment and hence the unpaired σ electrons were produced. And another reason is that aromatic nucleus would also produce unpaired electrons because of the dehydrogenation under heat-treatment. But as the carbonizing temperature ascends, the condensation reaction resulted in the increase of aromaticity, enlargement of condensed poly-cyclic layer and lead to the decline of the concentration of free radicals in the system. In Table 2, all values of g factors are close to that of free electron ($g_e=2.0023$), which are still belonged to the range of localized electrons. These specimens exhibited the paramagnetism performance, but not ferromagnetism. When the sample was heated up to 500°C , not only the concentration of free radical increased, the width of peak extended as well, indicating the existence of certain interactions between free radicals [7].

The molecule shape of Pyrene is like a round disk and its planeness is very high. So it is favorable to form a relatively regular orientation in the process of bridge jointing a pyrene molecule with a benzaldehyde molecule. The asymmetrical distribution of substituents resulted in a specific orientation of tri-aryl methyl radicals. A methenyl is surrounded by two pyrene rings and a benzene ring in the tri-aryl methyl structure. Therefore, tri-aryl methyl radical is relatively stable. If mutual magnetism occurred between radicals, the whole system would display magnetism. In summary, tri-aryl methyl structure is the intrinsic characteristic for magnetic behavior of the specimen.

Conclusions

(1) Under the catalysis of Para-toluene sulfonic acid, the pitch resin with tri-aryl methyl structure can be synthesized from Pyrene and benzaldehyde in low temperature.

(2) The B-stage pitch resin synthesized from pyrene and benzaldehyde, possesses high concentration of tri-aryl methyl radical after carbonization. It is proved that the tri-aryl methyl structure is the intrinsic characteristic for the magnetic behavior of the specimen.

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