



Polypropylene Fibre Grafted Styrene-divinylbenzene Copolymers Post-cross-linked with Cyanuric Chloride

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ABSTRACT

A preparation method for a permanently porous functionalized post-cross-linked polymer fibre is developed by chemical transformation of polypropylene fibre grafted styrene-divinylbenzene. The fibre post-cross-linking method involved the preparation of rigid three-dimensional networks in the entire polymer fibre and changing its specific surface area. As a cross-linker, cyanuric chloride was used in presence of a Friedel-Crafts catalyst. The effects of several important factors, e.g., reaction temperature, reaction time, catalyst type, and material ratio on Friedel-Crafts reaction were investigated in detail and the optimal synthetic conditions of post-cross-linked polymer fibre were obtained. Under optimal synthetic condition, the specific surface area of the post-cross-linked polymer fibre could be 58.16 m²/g, over 900 times the initial polymer fibre. Compared with the initial fibre, the post-cross-linked polymer fibre shows high specific surface area, large pore volume, abundant pore structure, and excellent adsorption property for organic vapours, as well. The experimental results showed that the adsorption capacity for organic vapours (methanol, benzene, and toluene) on the post-cross-linked polymer fibre was increased to about 3 times of that of the initial fibre. The adsorption capacity was related not only to the size of the pore network but also to the molecular size of organic vapours. The post-cross-linked polymer fibre has larger adsorption capacity for benzene than for the other organic vapours studied.

Key Words:

fibre;
Friedel-Crafts reaction;
cyanuric chloride;
surfaces;
adsorption.

INTRODUCTION

Three-dimensional polystyrene networks serve as the basis of various sorbents widely used both in laboratory practice and industrial technology. Simplicity of synthesis, availability of initial materials, the possibility of extensive variation in physical structure and therefore the operational properties of sorbents, has made polystyrene networks to earn much-deserved popularity. At present, these polymeric networks

can be divided into three large groups. The first group consists of homogeneous networks, which are styrene copolymers with divinylbenzene or other divinyl monomers, obtained by the radical copolymerization of monomers in the absence of a solvent. The second group consists of heterogeneous networks, which have interpenetrating networks as well as macroporous structures. They are

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obtained by the copolymerization of styrene with a relatively large amount of divinylbenzene in the presence of an inert diluent which dissolves the monomers but precipitates the growing copolymer.

The third group consists of hypercross-linked networks, the structure and properties of which differ in principle from the known types of homogeneous and heterogeneous networks. Such hypercross-linked polymers have been obtained by cross-linking linear polystyrene chains in solution or in swollen state using bifunctional compounds which react with phenyl rings via a Friedel-Crafts reaction. Three dimensional resins obtained in this way have been thoroughly studied [1-3].

Compared with resins, ion exchange fibres are new materials which have been rapidly developed in recent years. They have a number of advantages: greater exchange rate, shorter reclaiming time, ease of elution and the ability to be made in the form of filaments, staple fibre, nonwoven fabrics, cloths, bands, and many other textile forms. This creates new technological possibilities in the arrangement of ion exchange processes as well as opening new fields for the application of ion exchange processes [4-8]. To date, ion exchange fibres have been widely used in the fields of scientific research and commercial production. The most important and realistic application fields are water and air purification [9,10].

However, studies on three-dimensional networks in the fibrous form obtained by introducing additional cross-linked bridges by Friedel-Crafts reaction have rarely been reported [11-14]. Therefore, the synthesis of a post-cross-linked polymer fibre would be most desirable because the properties of its granular prototypes are well studied and their application fields are well defined.

In this study, a novel post-cross-linked polymer fibre has been prepared by the chemical transformation of polypropylene fibre grafted styrene-divinylbenzene. The aim of the fibre post-cross-linking method described in the present paper was to prepare a regular network in the whole polymer fibre and change its specific surface area. Using a post-cross-linking reaction, the new polymer fibre has been obtained under the formation of a permanently porous structure with higher specific surface area

compared to the initial fibre. The post-cross-linking of fibre is described using cyanuric chloride as a cross-linking agent. The post-cross-linked polymer fibre possesses a principally different structure and could offer new possibility for sorption, which is characterized by high adsorption capacity for organic vapours.

EXPERIMENTAL

Materials

The polypropylene grafted styrene-divinylbenzene (PP-ST-DVB) fibre was provided by the Henan University of Technology. Its specific surface area was approximately 0.06 m²/g. It was extracted with benzene before it was used. Nitrobenzene, cyanuric chloride, methanol, benzene, toluene, acetone and other chemicals were all analytical grade reagents.

Measurement

Specific Surface Area

A Brunauer-Emmet-Teller (BET) experiment for adsorption and desorption of nitrogen was performed by an automatic analyzer (American NOVA 2000e). From the nitrogen isotherms at -196°C, specific surface area was measured with an accuracy of 0.1% according to the BET theory. The pore volume and pore size distribution can be calculated by using the instrument.

Method for Measuring the Adsorption Capacity

Measurement apparatus of adsorption capacity is based on weighing method, wherein gas-solid adsorption plant is used. Sorbent mass was determined with an accuracy of ±0.1 mg, and fibre was introduced into quartzose spring balance. Prior to measurement, to eliminate any trace of pollutants, the fibre samples were desorbed at constant temperature under a high vacuum for 2 h. A total quantity of gas was admitted to the system at saturated vapour pressure. During adsorption, temperature was maintained at 20±0.02°C. The adsorption capacity of organic vapour on fibre at equilibrium can be calculated according to the weight changes of the fibre on quartzose spring balance in gas-solid adsorption plant.

Synthesis

The post-cross-linked polymer fibre was prepared by cross-linking the PP-ST-DVB fibre with a cross-linking agent according to the Friedel-Crafts reaction. A solution of quantitative cyanuric chloride in 15 mL of nitrobenzene was added quantitatively to the PP-ST-DVB fibre, and the mixture was held at room temperature for 12 h to facilitate swelling of the PP-ST-DVB fibre. The mixture was then cooled to 0-4°C, and a quantitative amount of catalyst was added in 10 mL of nitrobenzene. The mixture was placed in a vessel equipped with a reflux condenser, carefully stirred and was heated at 90-140°C for 10-24 h. Upon completion of the reaction, the fibre was washed with acetone, a mixture of acetone and 0.5 N HCl, water, and finally it was dried under vacuum at 60-80°C.

RESULTS AND DISCUSSION

Instead of PP-ST-DVB, as a traditional fibre, the cross-linking of styrene on polypropylene fibre chains is the distinguishing feature of the synthesis. Such cross-linked polymer has been obtained by cross-linking the styrene on polypropylene chains in swollen state using functional compounds. Cyanuric chloride, as the cross-linking reagent, reacts with phenyl rings via a Friedel-Crafts reaction forming a bridge between polymeric chains depicted in Figure 1. The cross-linking bridges formed by the above reaction have a long and rigid structure. They are capable of retaining the polypropylene chains at a significant distance from each other. Thus, three-dimensional networks were formed and the specific surface area of

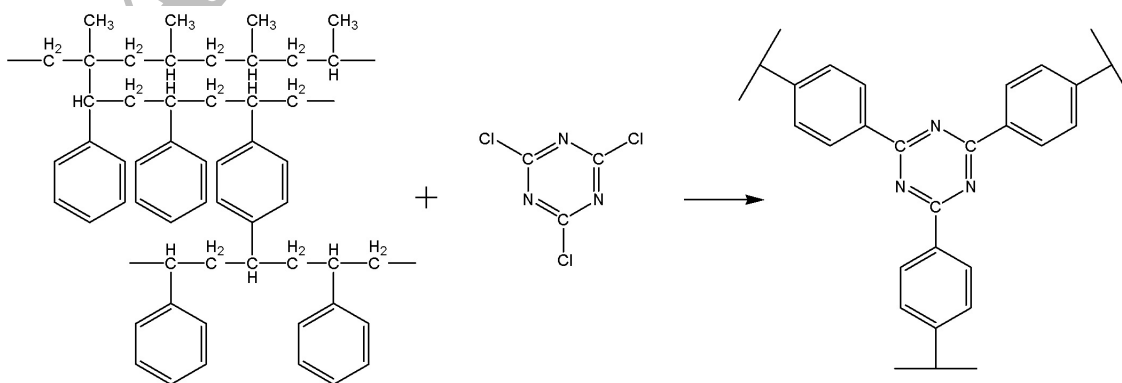


Figure 1. The scheme of the post-cross-linked polymer fibre.

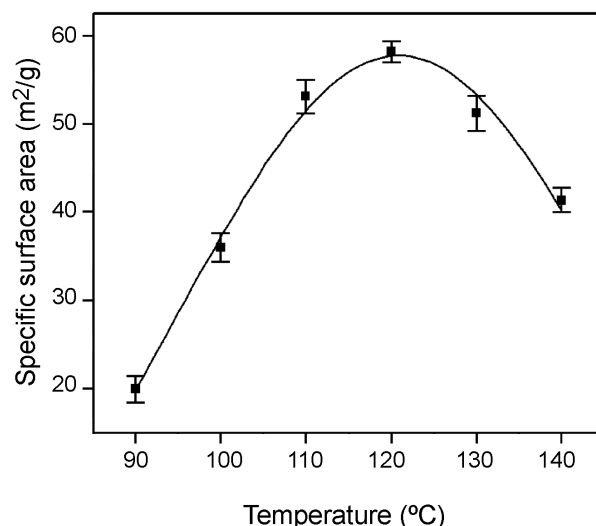


Figure 2. Dependence of the specific surface area of the post-cross-linked polymer fiber on reaction temperature.

the fibre increased significantly compared to the untreated fibre.

During the synthesis of the post-cross-linked polymer fibre, there are several important factors including reaction temperature, reaction time, type of catalyst, and material ratio which affect its specific surface area. The temperature dependence of the specific surface area of the post-cross-linked polymer fibre is shown in Figure 2. The reaction conditions were as follows: the described results were obtained by molar ratio of PP-STDVB/cyanuric chloride/catalyst = 1/0.63/1.26 and aluminium trichloride as catalyst were kept for 18 h. According to Figure 2, the temperature has a remarkable effect on the Friedel-Crafts reaction. The specific surface area of the post-cross-linked polymer fibre increased with the

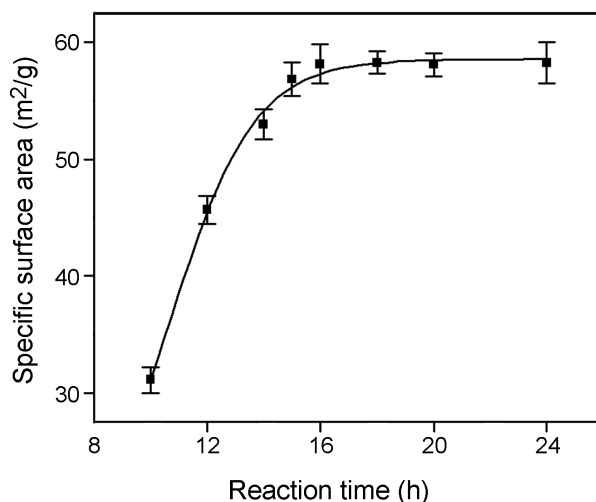


Figure 3. Dependence of the specific surface area of the post-cross-linked polymer fiber on time.

growing temperature, approaching the maximum at 120°C, then, began to decrease slowly. With increasing temperature of the Friedel-Crafts reaction, the reaction rate was increased, the degree of cross-linking of post-cross-linked structures and the length of cross-linking chains were all increased, and therefore, the specific surface area grew gradually. When the reaction temperature exceeded 120°C, the breaking rate of the polymer chains tended to increase which induced the decreases in specific surface area.

The dependence of the specific surface area of the post-cross-linked polymer fibre on reaction time is depicted in Figure 3. The reaction conditions as mentioned above are: the completion of the reactions at 120°C with the molar ratio of PP-ST-DVB/cyanuric chloride/catalyst=1/0.63/1.26 and aluminium trichloride used as a catalyst. As it is observed in Figure 3, an increase in specific surface area becomes evident with the prolonged reaction time. However, after 16 h, the specific surface area of the post-cross-linked polymer fibre tends towards a constant value.

The material ratio in the synthesis of the post-cross-linked polymer fibre also played an important role on the Friedel-Crafts reaction. The reaction conditions of the synthesis for when AlCl₃ was selected as a catalyst are briefly summarized in Table 1. From this Table, it can be observed that the specific surface area of the post-cross-linked polymer

Table 1. Effect of material ratio on the Friedel-Crafts reaction.

Amount of cross-linking agent (mol/mol PP-ST-DVB)	Specific surface area (m ² /g)
0.33	21.56
0.43	39.98
0.53	50.32
0.63	58.16
0.73	55.73
0.83	42.95

Reaction conditions: catalyst AlCl₃; temperature 120±0.1°C; time >18 h; amount of catalyst (mol/mol cross-linking agent) = 2.0

fibre increased with the growing amount of cross-linking agent, approaching a maximum, which then began to decrease. When the cross-linking agent was added in excess, it did not help to increase the specific surface area.

Some Lewis acids, e.g., AlCl₃, SnCl₄, and ZnCl₂ were used in all cases as the Friedel-Crafts catalysts. The molar ratios were the same as mentioned above and the detailed experiments are described in Table 2. As can be seen in Table 2, the catalytic activity of AlCl₃ is superior to that of SnCl₄ and ZnCl₂, thus, AlCl₃ has been applied as the optimal catalyst.

From the above studies, the optimal synthetic conditions of the post-cross-linked polymer fibre can be obtained. The post-cross-linked polymer fibre is synthesized with the molar ratio of PP-ST-DVB/cyanuric chloride/catalyst=1/0.63/1.26 and aluminium trichloride used as catalyst at 120°C for more than 16 h. Under this condition, the specific surface area of 58.16 m²/g for post-cross-linked polymer fibre can be attained. The specific surface area of the initial

Table 2. Effect of catalyst on the Friedel-Crafts reaction.

Catalyst	Specific surface area (m ² /g)
AlCl ₃	58.16
SnCl ₄	18.79
ZnCl ₂	5.65

Reaction conditions: temperature 120±0.1°C; time >18 h; molar ratio of PP-STDVB/cyanuric chloride/catalyst = 1/0.63/1.26

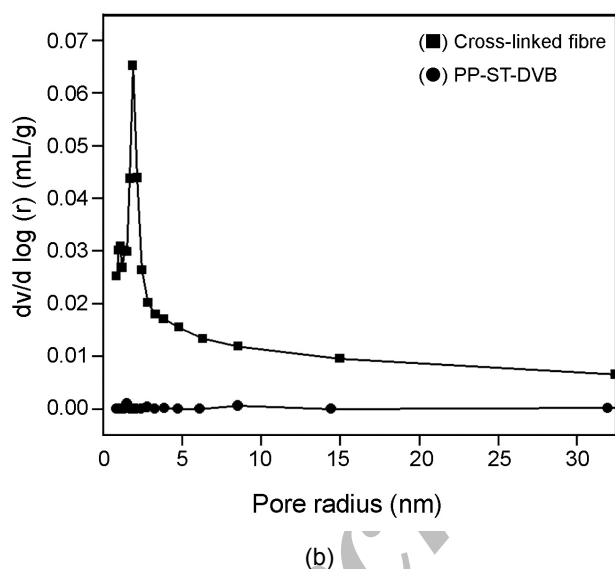
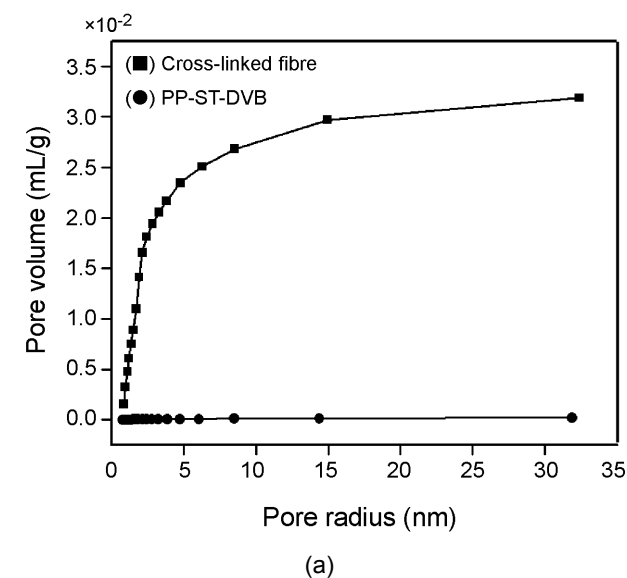


Figure 4. Plots of: (a) pore volume, and (b) pore size distributions for initial PP-ST-DVB and cross-linked fibres.

PP-ST-DVB is about $0.06 \text{ m}^2/\text{g}$. However, in contrast, the pore structure of the post-cross-linked polymer fibre was changed greatly after the Friedel-Crafts reaction. It has high specific surface area. With the long and rigid structure of the cross-linking bridges the polypropylene chains are retained at a significant distance from each other. Thus, three-dimensional networks formed have greater specific surface area.

Compared with PP-ST-DVB, the changes of the pore volume and the pore size distribution are illustrated in Figure 4. As it is shown in this Figure,

Table 3. The adsorption capacities (mg/g) of organic vapours on the fibres.

Fibre	Methanol	Benzene	Toluene
PP-ST-DVB	26.6	39.8	36.5
Cross-linked fibre	72.9	117.1	92.3

the pore volume of the fibre is changed and greatly increased by forming a high number of pores by the Friedel-Crafts reaction.

Because of the network structure of the post-cross-linked polymer fibre which differs in principle from the initial fibre, it can offer different sorption properties. The adsorption capacities of organic vapours on the fibres are listed in Table 3. It can be followed from Table 3 that the adsorption capacities of post-cross-linked polymer fibre are very high and have increased to about 3 folds. With the increase of the molecular size of organic vapours, the adsorption capacity of post-cross-linked polymer fibre tends to increase, and then it decreases. The adsorption capacity of the post-cross-linked fibre for benzene is larger than those for the other organic vapours studied.

Generally, adsorption is a surface phenomenon, therefore, the total surface area with respect to pore size and volume might be a criterion in determining its effectiveness in a particular application. The specific surface area of post-cross-linked polymer fibre is greatly increased and is more or less over 900 times of the initial fibre. Thus, the contact area between the adsorbates and the post-cross-linked polymer fibre is greatly increased in the course of adsorption. Therefore, a high adsorption can be gained. At the same time, the size of the network pore is helpful for adsorbing benzene vapour.

CONCLUSION

It is feasible that the post-cross-linked polymer fibre was synthesized by introducing additional cross-linking bridges according to the Friedel-Crafts reaction. The results show that the Friedel-Crafts reactions are obviously affected by reaction temperature, reaction time, catalyst, and material ratios. The effects were

investigated and the optimal synthetic conditions of the post-cross-linking of polymer fibre were achieved. Compared with PP-ST-DVB, the resulted post-cross-linked polymer fibre has a high specific surface area, a large pore volume, and abundant pore structure. Thus, the post-cross-linked polymer fibre is characterized by high adsorption capacity for organic vapours.

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