

## Synthesis and Adsorption Properties of a New Type of Functional Sorbents

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Received 5 August 2006; accepted 1 November 2006

### ABSTRACT

Three different novel sorbents were prepared by cross-linking polypropylene grafted styrene-divinylbenzene (PP-ST-DVB) fibre with monochloromethylether or *p*-xylylenedichloride or 1,4-bis-chloromethyldiphenyl according to Friedel-Crafts reaction. A series of synthesis tests were made and the effects of several important factors including reaction temperature, time, catalyst, and material ratio on the Friedel-Crafts reaction were investigated in detail. The optimal synthetic conditions of sorbents were obtained. Compared with PP-ST-DVB fibre, the sorbents have larger specific surface area, pore volume, pore radius and higher adsorption capacities for organic vapours. The adsorption capacities for organic vapours on the hypercross-linked sorbents were increased about 10 times. The adsorption capacities on the sorbents were related with the molecular length of cross-linking agents. The amounts absorbed on the sorbent 1, sorbent 2 and sorbent 3 can be reached to 428.6 mg/g for methanol, 471.9 mg/g for benzene, and 491.1 mg/g for toluene, respectively.

### Key Words:

hypercross-linked sorbents;  
Friedel-Crafts reaction;  
specific surface area;  
adsorption;  
organic vapours.

### 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 varying the physical structure within wide limits and therefore the operational properties of sorbents, have earned polystyrene networks much-deserved popularity. At present, the main types of polymeric networks

can be subdivided into three large groups. The first group consists of homogeneous networks, which are styrene copolymers with divinylbenzene (DVB) 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, which have interpenetrating networks as well as macroporous structures [1].

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They are obtained by the copolymerization of styrene with a relatively large amount of DVB 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 [2-5]. Three-dimensional networks resins obtained in these ways have been studied in greatest detail. Compared with resins, ion exchange fibres are new materials which have been rapidly developed in recent years. They have a great deal of advantages: the greater exchange rate, the shorter reclaiming time, easier to elute and can be made in a form of filaments, staple fibre, non-woven fabrics, threads, cloths, bands, braids and plenty of other textile items. This creates new technological possibilities in arrangements of ion exchange processes as well as opens new fields for the applications of ion exchange processes. So ion exchange fibres have been widely used in the fields of scientific research and commercial production. The most important and realistic fields of their applications are water and air purification [6-8]. But, up to now, the studies on three-dimensional networks in the fibrous form obtained by introducing additional cross-linking bridges according to the Friedel-Crafts reaction have not been reported yet. Therefore, the synthesis of hypercross-linked fibre would be most desirable because the properties of their granular prototypes are well-studied and fields of their applications are well defined [9,10].

The present paper deals with a new type of hypercross-linked sorbents which possess a principally different structure and it therefore offers new possibilities for sorption procedure from gaseous and liquid media.

## EXPERIMENTAL

### Materials

The polypropylene grafted styrene-divinylbenzene (PP-ST-DVB) fibre was provided by the Research

Institute of Organic Chemistry, Russia. It was extracted with benzene before use. Monochloromethylether (MCME) was distilled under its boiling ranges. 1,2-Dichloroethane was boiled over  $P_2O_5$  and distilled over fresh portion of the dryer. *p*-Xylyenedichloride (XDC) and 1,4-bis-chloromethyldiphenyl (CMDP) were used without additional purification.

Nitrobenzene, methanol, ethanol, benzene, toluene and other chemicals were all analytical reagents.

### Measurement

#### *Specific Surface Area*

A Brunauer-Emmet-Teller (BET) experiment for adsorption and desorption of nitrogen was performed by an automatic analyzer (American NOVA2000e). From the nitrogen isotherms at 77 K, specific surface area was calculated with an accuracy of 0.1% according to the BET theory. The average pore radius, pore volume, and pore size distribution can be calculated with an accuracy of 0.00001% by the DH method (American NOVA2000e).

#### *Method for Measuring the Adsorption Capacity*

The measurement apparatus of the adsorption capacity is based on the weight method. In this method, the gas-solid adsorption plant was used. The mass of sorbent was determined with an accuracy of  $\pm 0.1$  mg, and the sorbent was introduced into the quartzose spring balance. Prior to measurement, to eliminate any trace of pollutants, the sorbent was desorbed at constant temperature under a high vacuum for 2 h. The total quantity of gas admitted to the system was its saturated vapour pressure and the pressure was recorded using a pressure gauge. During adsorption, the temperature was maintained constant within  $\pm 0.02$  K by a refrigerated circulating thermostat and was measured with a T-type thermocouple. The adsorption capacity of organic vapour on the sorbent at equilibrium can be calculated according to the weight changes of sorbent on the quartzose spring balance in the gas-solid adsorption plant.

### Synthesis

#### *Hypercross-linked Sorbent 1*

A solution of quantitative MCME in 30 mL of 1,2-dichloroethane was added to quantitative PP-ST-DVB fibre, and the mixture was held at room temperature

for 12 h for swelling of the PP-ST-DVB fibre. Then the mixture was cooled to 273.15~275.15 K, the catalyst in 5 mL of 1,2-dichloroethane was added. The mixture was placed in a flask equipped with reflux condenser. The mixture was carefully stirred and it was heated at 313.15~353.15 K for 4~15 h, respectively. Upon accomplishing the reaction, the fibre was washed with acetone, a mixture of acetone, 0.5 N HCl, and water, and it was dried at 333.15~353.15 K under vacuum.

#### Hypercross-linked Sorbent 2

A solution of quantitative PP-ST-DVB fibre in 20 mL of nitrobenzene was added to a solution containing XDC and catalyst in 10 mL of nitrobenzene. The mixture was placed in a flask equipped with reflux condenser. The mixture was carefully stirred and it was heated at 353.15~393.15 K for 10~20 h, respectively. Upon accomplishing the reaction, the fibre was washed with acetone, a mixture of acetone, 0.5 N HCl, and water, and it was dried at 333.15~353.15 K under vacuum.

#### Hypercross-linked Sorbent 3

To a solution containing quantitative PP-ST-DVB fibre in 25 mL of 1,2-dichloroethane was added a solution containing CMDP and catalyst in 5 mL of 1,2-dichloroethane. The mixture was placed in a flask equipped with reflux condenser. The mixture was carefully stirred and it was heated at 333.15~383.15 K for 4~15 h, respectively. Upon accomplishing the reaction, the fibre was washed with acetone, a mixture

of acetone, 0.5 N HCl, and water, and it was dried at 333.15~353.15 K under vacuum.

## RESULTS AND DISCUSSION

Instead of a traditional fibre of PP-ST-DVB, cross-linking of styrene in the polypropylene fibre chains is the distinguishing feature of the synthesis. Such cross-linked polymers have been obtained by cross-linking styrene of polypropylene chains in swollen state using bifunctional compounds. As cross-linking agents, we have used MCME, XDC and CMDP. These compounds react with phenyl rings via Friedel-Crafts reaction. In this case, a bridge between two polymeric chains forms the following structure (Figure 1). The cross-linking bridges formed in the 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 fibre was greatly increased. Compared with PP-ST-DVB, the change of the pore volume and the pore size distribution are illustrated in Figure 2. As shown, the structure of fibre was changed by Friedel-Crafts reaction and a great many pores were formed. According to the elemental analysis in Table 1, the cross-linking agents were not grafted on PP-ST-DVB fibre by the forms of  $-\text{CH}_2\text{Cl}$  or  $-\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$  or  $-\text{CH}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$ , but the forms of  $-\text{CH}_2-$  or  $-\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2-$  or  $-\text{CH}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_2-$  cross-linking bridges were created by the Friedel-Crafts reaction.

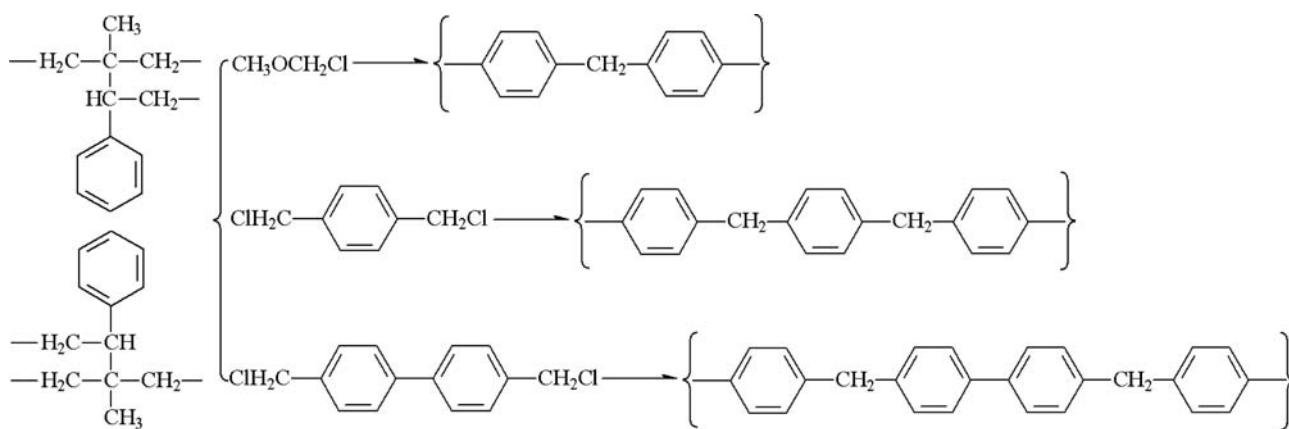
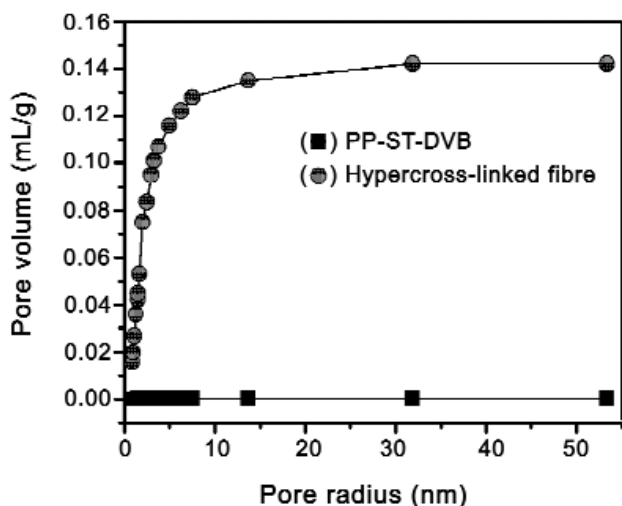
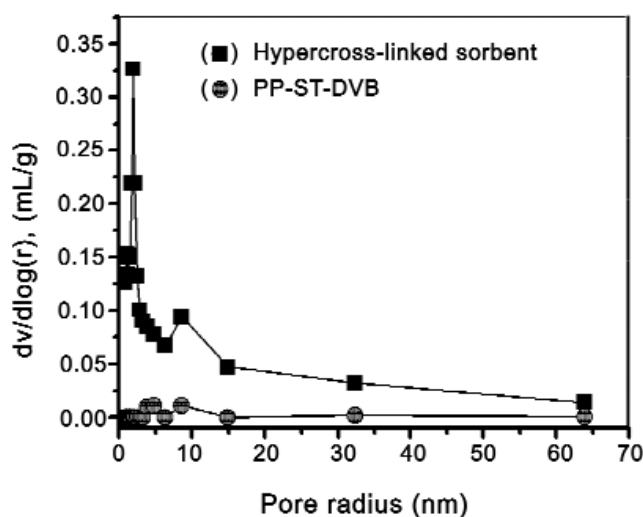


Figure 1. The schemes of sorbents.



(a)



(b)

Figure 2. (a) Pore volume, and (b) pore size distributions.

During the synthesis of the sorbents, there are several important factors including reaction temperature, reaction time, kinds of catalyst and material ratio which affect the specific surface area of the sorbents. The temperature dependence of the specific surface

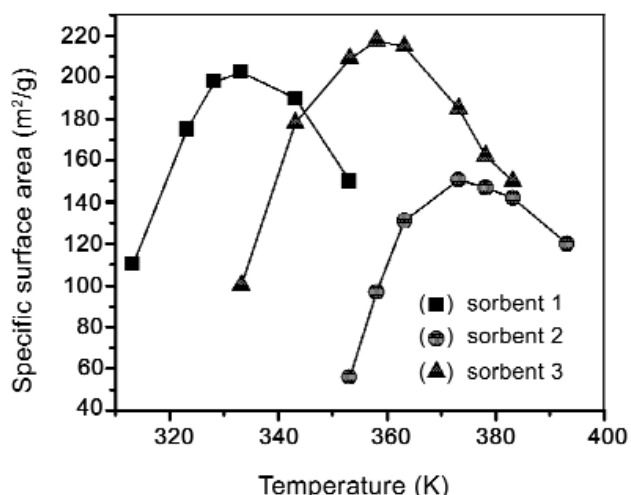
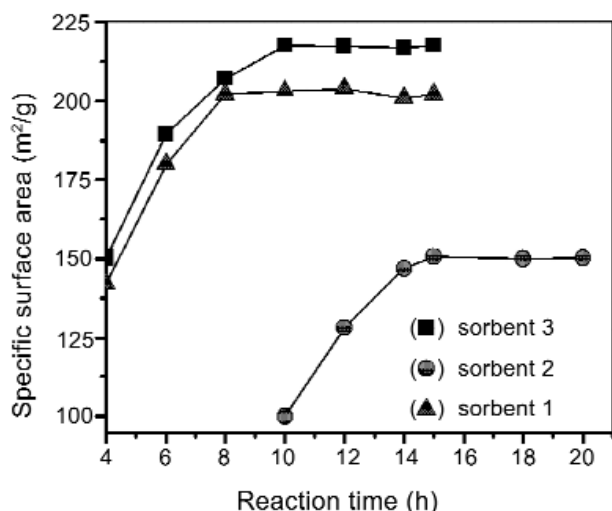


Figure 3. Dependence of the specific surface area of the hypercross-linked sorbents on reaction temperature.

area of hypercross-linked sorbents is shown in Figure 3. The reaction conditions were as follows: when the cross-linking agent was MCME, the described results were obtained in experiments where the molar ratio of PP-ST-DVB/MCME/catalyst = 1:0.60:0.45 and stannic tetrachloride as catalyst were kept for 12 h; when the cross-linking agent was XDC, the results were achieved in 18 h with aluminium trichloride as catalyst and the molar ratio of PP-ST-DVB/XDC/catalyst = 1:0.75:1.125 [11]; when the cross-linking agent was CMDP, the results were gained for 15 h in the molar ratio of PP-ST-DVB/CMDP/catalyst = 1:0.5:0.625, stannic tetrachloride used as catalyst. According to Figure 3, the temperature has a remarkable effect on Friedel-Crafts reaction. The specific surface area of the sorbents increased with the growing temperature, approaching the maximum at 333.15, 373.15, and 358.15 K, respectively, then, began to decrease slowly. With increasing temperature of Friedel-Crafts reaction, the reaction rate was increased, the degree of cross-linking of hypercross-linked structures and the length of cross-linking chain were all increased, and

Table 1. Elemental analysis of PP-ST-DVB and hypercross-linked sorbents.

Sorbent	Cross-linking agent	Carbon content (%)	Hydrogen content (%)	Chlorine content (%)	Weight increment (%)
PP-ST-DVB	-----	89.81	10.19	0.00	-----
Sorbent 1	MCME	90.19	9.81	0.00	3.89
Sorbent 2	XDC	90.99	9.01	0.00	37.51
Sorbent 3	CMDP	91.61	8.39	0.00	65.13



**Figure 4.** Dependence of the specific surface area of the hypercross-linked sorbents on time.

therefore, the specific surface area grew gradually. When the reaction temperature exceeded the certain value, the breaking rate of the polymer chains tended to increase which induced the decreasing of the specific surface area.

In Figure 4 the changes of the specific surface area of the hypercross-linked sorbents on reaction time are depicted. The reaction conditions were as follows: when the cross-linking agent was MCME, the reactions were completed with stannic tetrachloride used as catalyst, the molar ratio of PP-ST-DVB/MCME/catalyst = 1:0.60:0.45 at 333.15 K; when the cross-linking agent was XDC, the reactions were completed at 373.15 K with the molar ratio of PP-ST-DVB/XDC/catalyst = 1:0.75:1.125 and aluminium trichloride used as catalyst; when the cross-linking agent was CMDP, the reactions were completed at 353.15 K with molar ratio of PP-ST-DVB/CMDP/cat-

alyst = 1:0.5:0.625 and stannic tetrachloride used as catalyst. As it is seen from Figure 4, an increase in specific surface area with the prolonging time becomes more evident. But, after 8, 10, and 15 h, respectively, the specific surface area of the sorbents tends to a constant value.

AlCl<sub>3</sub>, SnCl<sub>4</sub>, and ZnCl<sub>2</sub> were used in all cases as the Friedel-Crafts catalysts. The molar ratios were the same as the above and the detailed experiments are described in Table 2. When the cross-linking agents were MCME and CMDP, the activeness of SnCl<sub>4</sub> was superior to that of AlCl<sub>3</sub> and ZnCl<sub>2</sub>; and while the cross-linking agent was XDC, AlCl<sub>3</sub> was tested as optimal catalyst.

The material ratio in the synthesis of hypercross-linked sorbents played an important role on Friedel-Crafts reaction. When the optimal catalyst was selected respectively, the reaction conditions of the synthesis are briefly summarized in Table 3. From this table, it is evident that the specific surface area of sorbents increased with the growing amount of cross-linking agent, approaching a maximum respectively, then, began to decrease. When the cross-linking agent was added in excess, it did not help in increasing the specific surface area.

From the above studies, the optimal synthesis conditions of sorbents can be obtained. When the cross-linking agent was MCME, the sorbent 1 can be synthesized with the molar ratio of PP-ST-DVB/MCME/catalyst = 1:0.60:0.45 and stannic tetrachloride used as catalyst at 333.15 K for more than 8 h; when the cross-linking agent was XDC, the sorbent 2 can be synthesized with the molar ratio of PP-ST-DVB/XDC/catalyst = 1:0.75:1.125 and aluminium trichloride used as catalyst at 373.15 K for more than

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

Cross-linking agent	Catalyst	Temperature (K)	Time (h)	Specific surface area (m <sup>2</sup> /g)
MCME	AlCl <sub>3</sub>	333.15	10	098.15
	SnCl <sub>4</sub>	333.15	10	202.31
	ZnCl <sub>2</sub>	333.15	10	120.74
XDC	AlCl <sub>3</sub>	373.15	18	150.64
	SnCl <sub>4</sub>	373.15	18	130.69
	ZnCl <sub>2</sub>	373.15	18	040.11
CMDP	AlCl <sub>3</sub>	358.15	12	153.37
	SnCl <sub>4</sub>	358.15	12	217.69
	ZnCl <sub>2</sub>	358.15	12	134.91

**Table 3.** Effect of material ratio on Friedel-Crafts reaction.

Cross-linking agent	Temperature (K)	Time (h)	Amount of cross-linking agent (mol/mol PP-ST-DVB)	Amount of catalyst (mol/mol cross-linking agent)	Specific surface area (m <sup>2</sup> /g)
MCME	333.15	10	0.40	0.75	110.33
	333.15	10	0.50		189.46
	333.15	10	0.60		201.37
	333.15	10	0.70		180.37
XDC	373.15	18	0.50	1.50	139.52
	373.15	18	0.75		150.21
	373.15	18	1.00		143.76
	373.15	18	1.25		109.81
CMDP	358.15	12	0.30	1.25	166.91
	358.15	12	0.50		215.38
	358.15	12	0.70		174.32
	358.15	12	0.90		117.42

**Table 4.** The structure parameters of sorbents.

Sorbent	Cross-linking agent	Specific surface area (m <sup>2</sup> /g)	Total pore volume (ml/g)	Average pore radius (nm)
PP-ST-DVB	-----	0.10	0.00061	0.00115
Sorbent 1	MCME	202.31	0.15172	1.79742
Sorbent 2	XDC	150.64	0.17229	2.29392
Sorbent 3	CMDP	217.69	0.20210	2.85672

**Table 5.** The adsorption capacities (mg/g) for organic vapours on the sorbents.

Sorbent	Methanol	Ethanol	Benzene	Toluene
PP-ST-DVB	032.0	039.1	048.9	042.2
Sorbent 1	428.6	316.6	202.3	175.4
Sorbent 2	284.4	375.6	471.9	297.5
Sorbent 3	251.8	267.9	368.2	491.1

15 h; and when the cross-linking agent was CMDP, the sorbent 3 can be synthesized with the molar ratio of PP-ST-DVB/CMDP/catalyst = 1:0.5:0.625 and stannic tetrachloride used as catalyst at 358.15 K for more than 10 h. Their relevant parameters are shown in Table 4. The results show that the pore structure of fibre was changed greatly after Friedel-Crafts reaction. In contrast with the initial PP-ST-DVB fibre, the sorbents have high specific surface area, pore volume and average pore radius. Because of the special structure of sorbents which differs in principle from the initial fibre, it can offer different sorption properties. The

adsorption capacities of organic vapours on the sorbents are listed in Table 5.

It follows from Table 5 that the adsorption capacities of hypercross-linked sorbents are very high. The adsorption capacity of the initial fibre only amounted to 30-50 mg/g, but the adsorption capacities of hypercross-linked sorbents were about 200-500 mg/g. It is seen that the adsorption capacities for organic vapours were increased to about 10 times, and they were related with the molecular length of cross-linking agents. With increasing size of organic vapours, the adsorption capacity of hypercross-linked sorbent 1 tended to

decrease; while, the result of sorbent 3 was contrary. The adsorption capacity on the sorbent 1 for methanol was the largest; however, the adsorption capacity on the sorbent 3 for toluene was the largest among the four types of organic vapours. When the cross-linking agent was XDC, the adsorption capacity for benzene was larger than that for else organic vapours.

As it is seen from Table 4, the specific surface area of PP-ST-DVB fibre is 0.1 m<sup>2</sup>/g. The maximum of specific surface area of hypercross-linked sorbents is 202.31, 150.64 and 217.69 m<sup>2</sup>/g, respectively. So the specific surface areas of hypercross-linked sorbents were greatly increased and were more than 1500 times of original fibre. So the contact area between the adsorbates and the hypercross-linked sorbents was greatly increased in the course of adsorption. Therefore the high degree of adsorption can be gained. The networks were formed during the Friedel-Crafts reaction. The sizes of the network pores were different because the molecular lengths of cross-linking agents were different. The CMDP chains are longer than the XDC chains and the XDC chains are longer than the MCME chains, so the larger the network pores, the more it adsorbs the big size organic vapour molecules. Generally speaking, the sorbent has optimal sorption capacity when the pore diameter of sorbent is about 2-6 times of the pore diameter of adsorbate. The above experimental data lead us to conclude that the relevant cross-linking agent in the course of synthesis may be selected according to the molecular size of adsorbate.

## CONCLUSION

It is feasible that the novel hypercross-linked sorbents were 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 ratio. The effects were investigated and the optimal synthetic conditions of sorbents were achieved. The specific surface area of sorbents, when calculated formally in terms of BET theory, reaches a value of 150-200 m<sup>2</sup>/g which is more than 1500-2000 times of original fibres.

The experimental data of this study lead us to con-

clude that hypercross-linked fibres as novel sorbents are effective in the adsorption of organic vapours. The hypercross-linked fibres are characterized by high adsorption capacity for organic vapours, which is related with the molecular length of cross-linking agents. The adsorption capacity for organic vapours on the hypercross-linked sorbents is increased to about 10 times. The amounts absorbed on the sorbent 1, sorbent 2, and sorbent 3 can be reached to 428.6 mg/g for methanol, 471.9 mg/g for benzene, and 491.1 mg/g for toluene, respectively.

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