

INVESTIGATION OF THE FRIEDEL-CRAFTS REACTION OF THE CHLOROMETHYLATED COPOLYMER OF STYRENE-DIVINYLBENZENE

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ABSTRACT

In the presence of Friedel-Crafts catalyst, the chloromethylated copolymer of styrene-divinylbenzene may react with each other and cross-link by itself. Thus a new type of polymeric adsorbent was obtained, and its structure was identified by its physical properties and infrared spectra. The Friedel-Crafts reaction is manifestly affected by the nature of the solvent, the kind and amount of catalyst used, reaction temperature and reaction time, etc.

The porous structure and physical properties of the adsorbent prepared have been investigated systematically. The adsorbent has high specific surface area (1000–1300 m²/g), porosity, narrow pore distribution, high skeleton density and good mechanical properties.

INTRODUCTION

In the early forties, Bevington et al.^[1] pointed out that the linear polystyrene reacted with 1,2-ethylene dichloride under the influence of Friedel-Crafts catalyst to form cross-linked polymers.

Since 1970, Davankov et al.^[2-4] studied systematically the reactions of linear polystyrene and low cross-linking copolymer of styrene and divinylbenzene with chloromethyl methyl ether, 1,4(dichloromethyl)benzene and 4,4'(dichloromethyl)biphenyl respectively under the influence of Friedel-Crafts catalyst and obtained cross-linked polymers.

Recently, Kunin et al. pointed out that the copolymer of chloromethylated styrene-acrylonitrile-divinylbenzene would give cross-linked product^[5-6] with high specific surface area when heated in the presence of Friedel-Crafts catalyst. In addition, Negre et al.^[7] also pointed out that the chloromethylated copolymer of styrene-divinylbenzene when heated with Friedel-Crafts catalyst would form cross-linked product by itself.

The authors found out earlier that chloromethylated copolymer of styrene-divinylbenzene would react itself under the action of Friedel-Crafts catalyst with heating and high specific

surface area product was obtained^[8]. In this paper, we studied this reaction in more detail.

SYNTHESIS AND CHARACTERIZATION OF THE STRUCTURES OF PRODUCTS

1. *Synthesis*

- (1) Preparation of copolymers and their chloromethylation^[9].
- (2) Cross-linking reaction of chloromethylated copolymer of styrene-divinylbenzene with Friedel-Crafts catalyst.

To a three-necked flask equipped with a condenser, thermometer and a stirrer, were added the chloromethylated copolymer beads, a definite amount of solvents and Friedel-Crafts catalyst, and then it was heated slowly with stirring. After 3—15 hours, the reaction was stopped and cooled to room temperature. The mother liquid was evaporated with water suction, the product washed and extracted with organic solvent.

2. *Characterization of structure of products*

The chlorine content of chloromethylated copolymer of styrene and divinylbenzene before and after the Friedel-Crafts reaction was analyzed. From Tables 1 and 2, it indicates that the chlorine content became less after the Friedel-Crafts reaction. The infrared analysis (Table 2), showed that the Friedel-Crafts reaction had taken place since the C—Cl absorption peak at 670 cm^{-1} disappeared after the reaction (Fig. 1a and 1b). This accounted for the fact that the amount of benzylchloride group in polymer was considerably decreased or nearly disappeared. In addition, the absorption peak at 1260 cm^{-1} due to vibration of the non-planar methylene group next to the chlorine atom, was also disappeared after the reaction.

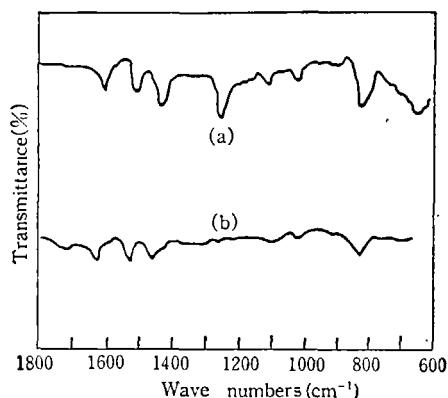


Fig. 1 Infrared spectra
(a) chloromethylated bead before Friedel-Crafts reaction;
(b) after Friedel-Crafts reaction.

FACTORS AFFECTING THE FRIEDEL-CRAFTS CROSS-LINKING REACTION

1. Effect of solvent

From Table 1 it indicated that the pore structures of polymeric adsorbent prepared were very different by using different solvents. It could be seen that the self cross-linking reaction was related to the dielectric constant and electrical conductance of the solvent used. The

Table 1 Effect of solvent on the Friedel-Crafts' cross-linking reaction*

No.	Name of solvent	Property of solvent**		Property of adsorbents				
		Dielectric constant (ϵ)	Electrical conductance (K)	Residual chloride content (%)	Specific surface area (m ² /g)	Apparent density (g/ml)	Skeletal density (g/ml)	Porosity (%)
1	Nitrobenzene	34.82 (25°C)	9.1×10^{-7} (25°C)	3.6	957	0.69	1.15	40
2	Ethylene tetrachloride	8.20 (20°C)	—	8.9	395	0.66	1.05	37
3	Ethylene dichloride	10.36 (25°C)	3×10^{-10} (25°C)	9.3	436	0.74	1.11	34
4	o-dichlorobenzene	9.93 (25°C)	—	9.9	380	0.72	1.25	42
5	Chlorobenzene	5.62	$< 1 \times 10^{-8}$ (0°C)	12.5	136	0.97	1.32	26
6	Dioxane	2.21 (25°C)	5×10^{-18} (25°C)	15.5	95	0.80	1.17	32

* The chlorine content of the initial chloromethylated copolymer was 17.8% and specific surface area was 53m²/g.

** Values taken in literature.

larger the dielectric constant and electrical conductance of solvent the higher was the degree of self cross-linking of the chloromethylated copolymer of styrene-divinylbenzene.

2. Effect of catalyst

The effect of catalyst on the Friedel-Crafts' cross-linking reaction was shown in Table 2. The effect of different amount of catalyst on Friedel-Crafts' cross-linking reaction was shown in Fig. 2. The zinc chloride, aluminum chloride, ferric chloride and stannic chloride are good catalysts for the cross-linking reaction. When nitrobenzene or nitroethane was used as the solvent, zinc chloride showed the highest activity. When o-dichlorobenzene was used as

the solvent, the activity of the zinc chloride was lower.

Table 2 The effect of different catalysts on Friedel-Crafts cross-linking reaction*

No.	Catalyst	Solvent	Temperature (°C)	Property of adsorbents	
				Chloride content (%)	Specific surface area (m ² /g)
1	Ferric chloride	Nitroethane	112—113	1.1	882
2	Zinc chloride	Nitroethane	112—116	1.2	842
3	Stannic chloride	Nitroethane	111	3.8	490
4	Aluminum chloride	Nitroethane	110	—**	—**

* Chlorine content of the initial chloromethylated beads: 20.8%, specific surface area: 20.8 m²/g.

** Reaction does not take place since aluminum chloride is insoluble in nitroethane.

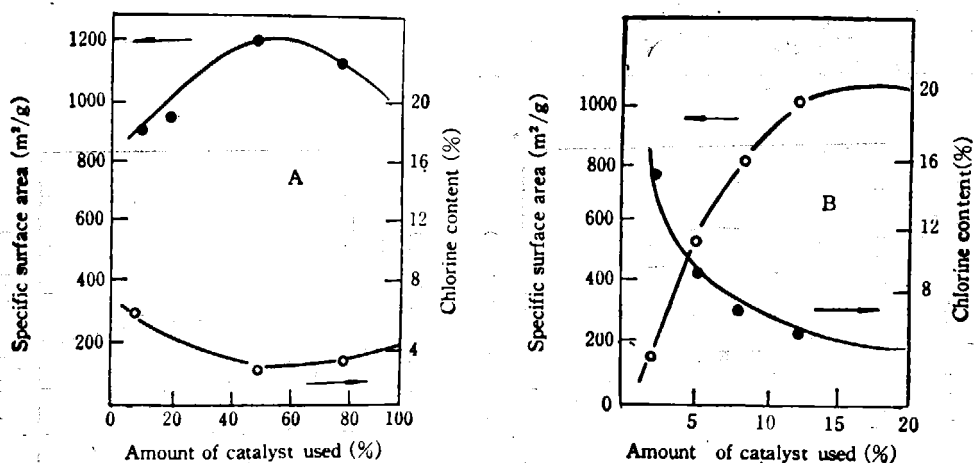


Fig. 2 Effect of amount of catalyst (ZnCl_2) on Friedel-Crafts reaction
A: Nitrobenzene as solvent; B: Nitroethane as solvent.

3. Effect of temperature

Experiments indicated that temperature effected the Friedel-Crafts reaction prominently (Fig. 3). When nitrobenzene was used as solvent and the reaction temperature raised to a certain degree, the resin thus prepared has high specific surface area i.e. 1000—1300 m²/g and low chlorine content. Its porosity was 40—60%. When o-dichlorobenzene was used as the solvent, the reaction underwent slowly. However, when the reaction temperature went up to the boiling point of o-dichlorobenzene, the specific surface area and porosity came up to 1000 m²/g and 55—60% respectively.

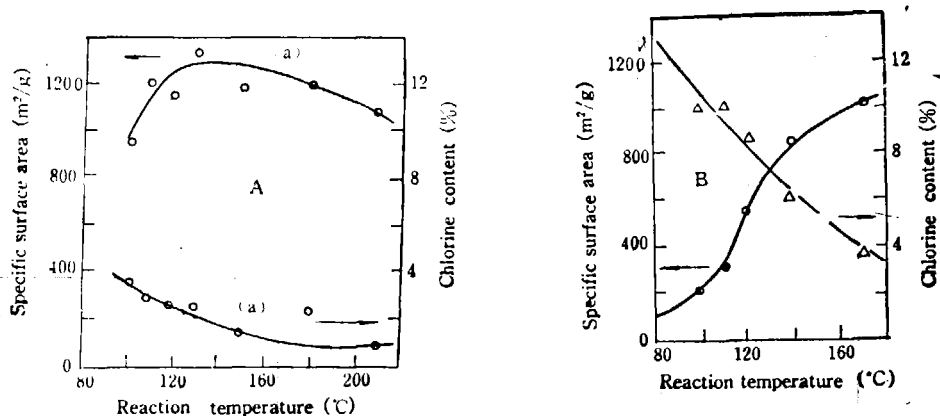


Fig. 3 Effect of temperature on Friedel-Crafts cross-linking reaction
A: Nitrobenzene used as solvent; B: o-dichlorobenzene used as solvent.

4. Effect of time

When nitrobenzene or nitroethane was used as the solvent and zinc chloride as catalyst, the reaction took place very fast if the temperature was kept above 100°C. In general, it took only 7 to 8 hours for the completion of reaction (Fig. 4).

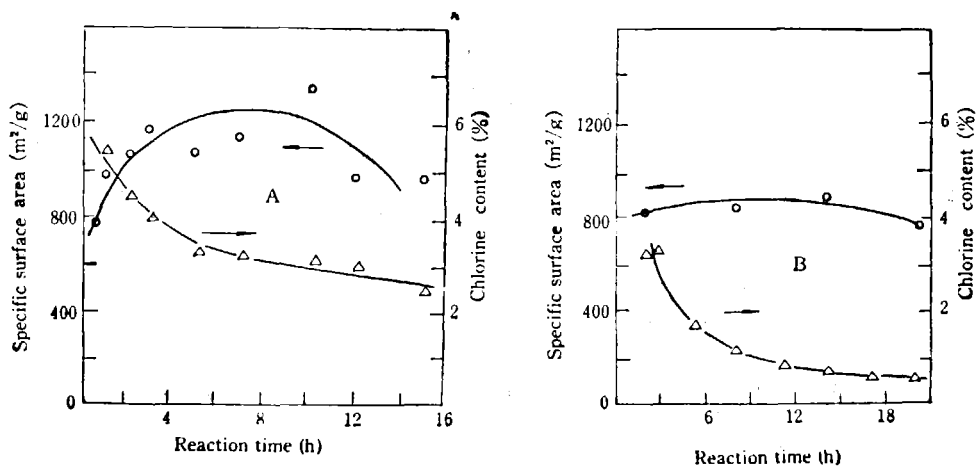


Fig. 4 Effect of time on Friedel-Crafts cross-linking reaction
A: Nitrobenzene used as solvent; reaction temperature, 120°C;
B: Nitroethane used as solvent; reaction temperature, 112–116°C.

PROPERTIES OF POLYMERIC ADSORBENT

1. Swelling property of polymeric adsorbent in organic solvents

If the swelling coefficient of the resin in water was taken as unity, the swelling ratios of

resins in different solvents were measured as shown in Table 3.

Table 3 The swelling ratios of resins in different organic solvents

No.	Solvent	Diaion HP-20* (Japan)	MH100	MH103	MH110	MH130	MH180
1	Nitrobenzene	—	1.55	1.54	1.37	1.50	1.29
2	Ethylene dichloride	1.30	1.55	1.20	1.12	1.18	1.22
3	Ethylene tetrachloride	—	1.38	1.24	1.18	1.13	1.10
4	Benzene	1.33	1.29	1.10	1.09	1.20	1.13
5	Toluene	1.31	1.38	1.12	1.18	1.12	1.10
6	Hexane	1.31	1.36	1.19	1.12	1.10	1.10
7	o-dichlorobenzene	—	1.39	1.09	1.16	1.15	1.13
8	Ketone	1.32	1.30	1.05	1.00	1.10	1.05
9	Dioxane	1.32	1.33	1.10	1.00	1.11	1.09
10	Methanol	1.26	1.25	1.08	1.05	1.02	1.04
11	Water	1.0	1.0	1.0	1.0	1.0	1.0

* Values taken in literature.

2. Mechanical strength of polymeric adsorbents

The mechanical strength of polymeric adsorbents was measured by the weight pressure equipment^[10]. The results were shown in Table 4.

Table 4 Mechanical strength of the dry polymeric adsorbents

No.	Name of adsorbent	Property of adsorbent	
		Diameter of adsorbent beads (mm)	Tolerance of twenty beads of maximum weight when adsorbent began to break (g)
1	MH103	0.63	800
2	MH110	0.63	820
3	MH130	0.63	690
4	MH180	0.63	780
5	D ₁₃ *	0.63	400
6	Amberlite XAD-2 (U. S.)	0.63	600
7	BAC (Japan)	0.63	880

* Macroporous resin produced in China.

In addition, the MH103 and MH180 were put into water, heated to 100°C and stirred at this temperature at the rate of 200 rpm for 24 hours. After the test, it was found that no bead was broken.

The authors also carried out the tolerance test for MH110 through which sufficient amount of 1*N* alkaline and 1*N* acid and water were perforated alternatively in a column for 800 cycles. From such experiments, it was found no bead was broken.

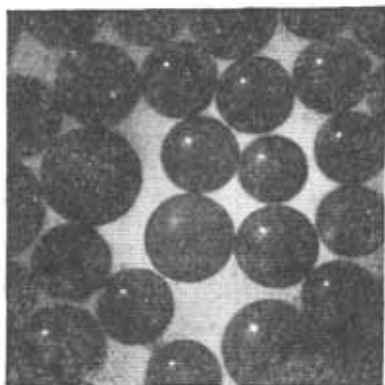


Fig. 5 Microscopic picture of MH110 adsorbent (40 $\times$)

From the above test, it was known that the adsorbent resin possesses good mechanical strength and physical-chemical stability.

3. Pore structure of the adsorbent

The scanning electronic microscope picture of polymeric adsorbent MH110 on JSM-25S.

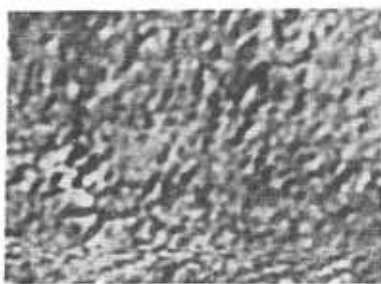


Fig. 6 SEM picture of MH110 (20,000 $\times$)

The specific surface areas of the polymeric adsorbents were measured with simple BET method. Their apparent densities and skeletal densities were determined by pycnometer and heptane swelling method. Then the porosity was calculated (Table 5).

The average pore diameter and pore distribution were measured by the Japanese 3010 X-ray diffraction spectroscopic machine and the American Quantachrome scanning porosimeter respectively (Table 6 and Fig. 7).

Table 5 Pore structure of the polymeric adsorbent

Name of adsorbent	Properties of adsorbent				
	Apparent density (g/ml)	Skeletal density (g/ml)	Specific surface area (m ² /g)	Porosity (%)	Colour and appearance of adsorbent
MH103	0.69	1.15	957	40	Brown spherical beads
MH110	0.52	1.22	1208	57	Deep brown spherical beads
MH120	0.52	1.29	1168	60	"
MH130	0.50	1.37	1369	64	Black glistening spherical beads
MH150	0.54	1.28	1164	58	"
MH180	0.53	1.31	1202	58	"
MH210	0.55	1.27	1074	56	"

Table 6 The average pore diameter and approximate pore distribution of adsorbents were measured by the X-ray diffraction spectroscopic method*

Property of adsorbent No. Name of adsorbent		Specific surface area <i>S</i> (m ² /g)	Average pore diameter $\bar{D}$ (Å)	Approximate pore distribution									
				<i>D</i> ₁ (Å)	<i>W</i> ₁ (%)	<i>D</i> ₂ (Å)	<i>W</i> ₂ (%)	<i>D</i> ₃ (Å)	<i>W</i> ₃ (%)	<i>D</i> ₄ (Å)	<i>W</i> ₄ (%)	<i>D</i> ₅ (Å)	<i>W</i> ₅ (%)
1	MH103	957	109	35	69.3	84	6.5	164	6.1	258	6.6	454	11.5
2	MH110	1208	89	33	58.9	74	17.2	143	9.5	219	5.0	339	9.8
3	MH120	1168	94	35	54.4	75	21.2	158	10.8	247	6.4	360	7.3
4	MH180	1202	41	20	84.6	62	5.2	112	3.8	174	2.6	312	3.8
5	Diaion HP-20 (Japan)	718	93	43	59.6	87	21.0	168	10.1	232	6.7	585	3.0
6	BAC (Japan)	1294	31	23	89.0	61	9.0	128	1.5	220	0.8	419	0.4

* $D_x(\text{Å})$ represents the average pore diameter of each fraction and $W_x(\%)$ represents the percentage of each fraction, where $x=1$ to 5 represents fraction 1—5.

From Table 6 and Fig. 7, it indicates that the adsorbents prepared above possess small average pore diameter and narrow pore distribution, which are measured by means of small angle X-ray diffraction and scanning porosimeter respectively and got nearly the same results, i.e., the average pore diameter ($\bar{D}$) of MH 110 being 89 Å by the former method and 90 Å by the latter method.

As mentioned above, this kind of adsorbent possess very good adsorption property which can adsorb organic matters as well as the active charcoals, and the adsorbed matter can be

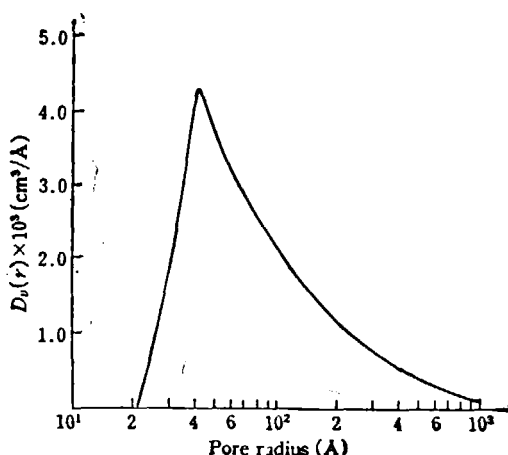


Fig. 7 The pore distribution curve of the MH110 measured with the scanning porosimeter

eluted completely. For this reason, after regeneration the polymeric adsorbents can be used again and again while the active charcoals can not.

CONCLUSION

The polymeric adsorbents we made possess good adsorption and efficient regenerative properties. They have good stable physical properties, high specific surface area, high porosity and high density, narrow pore distribution and low average pore diameter.

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