

INFLUENCE OF FUNCTIONAL GROUP REACTIONS ON THE PORE STRUCTURE OF MACROPOROUS CROSSLINKED POLYSTYRENE RESINS*

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ABSTRACT

The change of the pore structure of styrene-divinylbenzene copolymer caused by the presence of the functional group has been described in this paper. The result indicates that the average pore radius, pore volume and surface area were reduced after the introduction of the functional groups. However, the surface area of the resin containing $-\text{NH}_2$ or $-\text{NHCH}_3$ group and treated with water and isopropyl alcohol was increased prominently in comparison with that of the matrix copolymer.

When the strongly polar ion exchange resin absorbs water, its pore diameter increases sharply. But the pore diameter of the weakly polar ion exchange resin does not change very much when it absorbs water gradually.

The production of macroporous resins is an important step in the development of ion-exchange resin which is widely used in industry and research. Macroporous ion-exchange resins are usually synthesized by the introduction of functional groups into the macroporous copolymer. The pore structure has important influence on the property of ion-exchange resin which depends on the matrix copolymer and the kind of functional group introduced.

The change of pore structure caused by the introduction of some functional groups had been studied^[1-4]. It was proved that both the introduction of functional group and the solvent treatment may influence the pore structure. That is why the results obtained by different authors were not consistent. Another factor which affects the physical property is that the pore structure of dry resin is different from that of the resin in solvent. The measurement of the pore structure of the resin is usually carried out in dry state. It is not clear about the pore structure of the ion-exchangers used in liquid media, and so we can not design the pore structure of the copolymer matrix to meet a special purpose.

The purpose of this work is to study the influence of functional groups on the pore structure of macroporous resins and to examine the measurement methods for pore structure of macroporous resins under conditions close to that of the actual application, i.e. in liquid media.

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EXPERIMENTAL

The macroporous copolymer used was prepared by copolymerization of styrene and divinylbenzene (6%) in the presence of a solvent (petrol, in amount equivalent to 100% of monomers). All the ion-exchange resins were made from this copolymer by conventional method. The properties of these resins were listed in Table 1.

Table 1 Property of some resins containing functional groups

Resin	$-\text{NH}_2$	$\begin{array}{c} \text{H} \\ \\ -\text{NCH}_3 \end{array}$	$-\text{N}(\text{CH}_3)_2$	$-\text{N}(\text{CH}_3)_3^+$	$-\text{SH}$	$-\text{N}(\text{CH}_2\text{COOH})_2$	$-\text{SO}_3\text{H}$
Exchange capacity (meq/g)	5.39	4.60	4.51	4.11	3.75	1.00	5.16
H ₂ O content (%)	61.6	42	51	75.7	38.5	66	72.8

The macroporous copolymer thus prepared was washed with butyl acetate and ethanol in a column and the cross-linked chloromethyl polystyrene washed successively with acetone and ethanol. The other resins containing functional groups were washed successively with water, ethanol, benzene and heptane or water and isopropyl alcohol. Thereafter, all the resins were dried in a vacuum drier at 40°C for 8 hours. The measurement of the surface area was carried out with B.E.T. equipment and the distribution of pore radius was measured with Quantachrome scanning porosimeter. The specific skeleton volume and the specific apparent volume were determined with specific gravity bottle.

The pore parameters of the resins soaked in solvent were measured by the method as shown in literature^[7].

RESULTS AND DISCUSSION

1. Dry resins

Because of the limitation of the measurement method, at present, the pore parameters of commercial resins were all measured in the dry state. The pores of wet resins shrank significantly when they were dried. Therefore, we have to use appropriate pretreatment method in order to allow the smallest shrinkage of the pores of the resin.

After treatment with the above-mentioned method, the pore parameters of the resins were changed as listed in Table 2.

From Table 2, it indicates that after the group, $-\text{SH}$ or $-\text{CH}_2\text{Cl}$, has been introduced into the macroporous copolymer of styrene-divinylbenzene, the surface area per unit weight of the matrix copolymer does not change remarkably. On introduction of such group as $-\text{N}(\text{CH}_3)_2$, $-\text{N}(\text{CH}_2\text{COOH})_2$, or $-\text{SO}_3\text{H}$ into the copolymer, the reduction of surface area is very remarkable. On the other hand, the surface areas of the $-\text{NH}_2$ and $-\text{NHCH}_3$ resins are much greater than that of the initial copolymer.

According to the results obtained by Laskorin^[11], when $-\text{CH}_2\text{Cl}$ group is introduced

Table 2 Pore parameters of dry resins

Resin	Copolymer		$-\text{CH}_2\text{Cl}$		$-\text{NH}_2$	$-\text{NHCH}_3$	$-\text{N}(\text{CH}_3)_2$	$-\text{N}(\text{CH}_3)_3^+$	$-\text{SH}$	$-\text{N}(\text{CH}_2\text{COOH})_2$	$-\text{SO}_3\text{H}$
Surface area (m ² /g)	108	a	70	c	126	115	53	26	85	50	15.3
				d	113	67	47	1.1	89	45	0.8
		b	103.5	c	150.3	144	71.8	41.3	103.2	58.5	32.7
				d	134	84	63.8	1.7	108	52.7	1.8
Skeleton volume (ml/g)	0.92	a	0.80	c	0.84	0.85	0.88	0.82	0.82	0.78	0.71
		b	1.05		1.00	1.05	1.19	1.17	1.00	0.98	1.21
Apparent volume (ml/g)	1.73	a	1.26	c	1.31	1.30	1.29	0.93	1.30	1.12	0.77
		b	1.65		1.56	1.61	1.75	1.33	1.58	1.41	1.31
Pore volume (ml/g)	0.81	a	0.46	c	0.47	0.45	0.41	0.11	0.48	0.34	0.06
		b	0.60		0.56	0.56	0.56	0.16	0.58	0.43	0.10
Average pore radius (Å)	243		116	c	73	78	76.5		91.5	79	41
				d	72.8	77	72.3	—	90.8	—	39.4

a. Per unit weight of dry resin;

b. Per unit weight of matrix copolymer;

c. Washed with H₂O and iso-C₃H₇OH;d. Washed with H₂O, C₂H₅OH, C₆H₆, and C₇H₁₄.

into the copolymer, the surface area increased about 50%. This is inconsistent with our results. Since we have used a different pretreatment method which reduced the shrinkage of the pores of the copolymers and thus larger surface areas were obtained. This fact shows that the choice of appropriate solvents for the washing is very important.

Brutskus and Leikin^[2,8] studied the change of pore structure when some groups were introduced into the copolymer. The results we obtained indicate that the pore structures changed greatly when different groups were introduced into the copolymer and the extent of change in pore structure depended on the method of pretreatment and the nature of the functional groups introduced.

The introduction of such groups as $-\text{NH}_2$, or $-\text{NHCH}_3$, with low polar and hydrophilic properties, causes the formation of more micropores. Thus the surface area increases.

However, the micropores do not contribute much to the pore volume. On the other hand, the pores of the resins containing functional groups shrank greatly after they were dried. So the pore volume reduced (Table 2).

Functional groups such as $-\text{N}(\text{CH}_3)_2$, $-\text{N}(\text{CH}_3)_3^+$, $-\text{SO}_3\text{H}$, or $-\text{N}(\text{CH}_2\text{COOH})_2$ with higher polarity increase the shrinkage of the macropores because they increase the acting

force between the chains of the copolymer. Although the polarity of pure $\text{—N(CH}_3)_2$ is not

high, yet it may form some quaternary groups such as $\text{N}^+(\text{R})(\text{CH}_3)_3 \text{Cl}^-$ which is a strongly polar

compounds. As a result, both the pore volume and the surface area are decreased (see Table 2).

Fig. 1 and Table 2 show that the pore volumes of resins containing polar groups possess smaller values as the pore radii are smaller. There are attractive forces between the polar groups of polymer molecules, and the larger the polarity of the group, e.g. $\text{—SO}_3\text{H}$, the smaller is the pore volume.

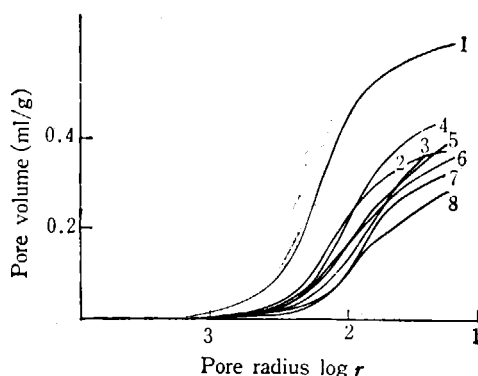


Fig. 1 Accumulative curves of pore volume of some dry resins

1 Copolymer	2 $\text{—CH}_2\text{Cl}$	3 —NH_2
4 —SH	5 —NHCH_3	6 $\text{—N(CH}_3)_2$
7 $\text{—N(CH}_2\text{COOH)}_2$	8 $\text{—N(CH}_3)_3$	

2. Resins containing solvent

At present, there are only a few papers^[5,6] concerning the investigation of pore structures of wet resins. The non-solvents do not swell resin beads. They can only penetrate into the pores of resins.

If resins were swollen with good solvent and then washed with non-solvent, the pore structure of the resins was different from that of the dry resins. Some results measured are listed in Table 3.

From Table 3 we can see the pore volume and the apparent volume of the resins which contain a non-solvent (heptane) are much larger than that of the dry resins. This is because that the non-solvent prevents the pores from shrinkage during the drying process of the resins.

Ion exchange resins swell in aqueous media and their pore structures are different from both the dry resins and the resins soaked in non-solvent.

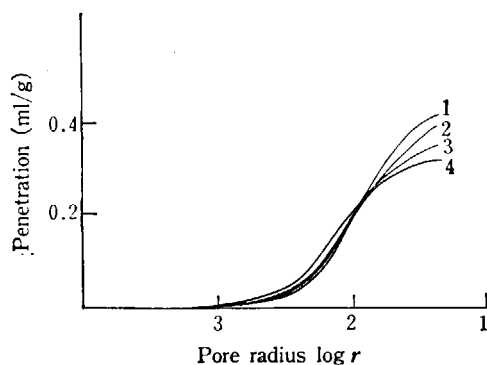
We had measured the distributions of pore radii of some ion-exchangers which have absorbed different amount of water. The resins with absorbed water were first frozen to about -50°C ; then mercury was filled into the sample tube under vacuum and the distribution of pore radius was measured at room temperature. The results obtained are shown in Figs. 2, 3 and 4.

Table 3 Pore volume and specific volume of resin containing heptane

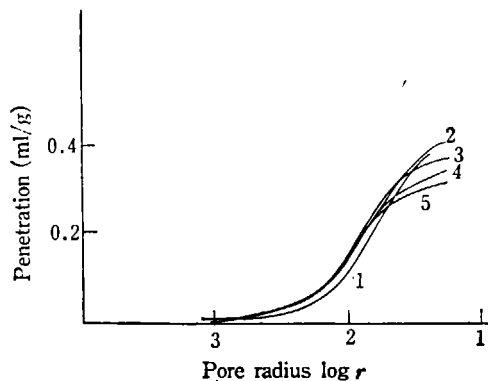
Resin	Copolymer	$-\text{CH}_2\text{Cl}$	$-\text{NH}_2$	$-\text{N}(\text{CH}_3)_2$	$-\text{N}(\text{CH}_3)_2$	$-\text{N}(\text{CH}_3)_3^+$	$-\text{SH}$	$-\text{N}(\text{CH}_2-\text{CCCH}_2)_2$	$-\text{SO}_3\text{H}$
Pore volume (ml/g)	1.16	a0.84 b1.10	1.29 1.54	0.66 0.83	0.63 0.85	0.79 1.25	0.80 0.97	0.75 0.88	0.17 0.29
Apparent volume (ml/g)	2.04	a1.63 b2.13	2.15 2.57	1.52 1.91	1.41 1.91	1.62 2.57	1.61 1.96	1.58 1.85	0.80 1.52
Skeleton volume (ml/g)	0.88	b1.04 a0.79	1.04 0.86	1.08 0.87	1.06 0.78	1.32 0.83	0.99 0.81	0.97 0.83	0.72 1.23

a. Per unit weight of dry resins;

b. Per unit weight of matrix copolymer.

Fig. 2 Accumulative curves of distribution of pore radius and pore volume of $-\text{SH}$ resin

Water content (%): 1 0.0; 2 5.5; 3 11.8; 4 15.1.

Fig. 3 Accumulative curves of distribution of pore radius and pore volume of $-\text{NH}_2$ resin

Water content (%): 1 0.0; 2 10.3; 3 15.8; 4 21.2; 5 25.5.

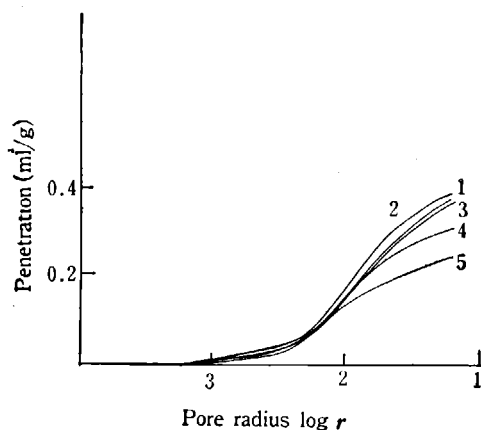


Fig. 4 Accumulative curves of distribution of pore radius and pore volume of $-\text{NHCH}_3$ resin
Water content (%): 1 0.0; 2 9.8; 3 5.8; 4 17.2; 5 27.9.

From Figs. 2, 3, 4, it follows that, when resins with $-\text{NH}_2$, $-\text{NHCH}_3$ or $-\text{SH}$ group have absorbed water up to 25.5%, 27.9% and 15.1% respectively, the pore radius did not change greatly, when the quantity of the water absorbed exceeds a certain value, the pore volume reduced progressively. The pore structure of this kind of resins which have absorbed a definite quantity of water was in a similar condition as that of the dry resins. For this reason, their pore diameter is approximately equal to that of the dry resin.

When the ion exchange resins containing strong polar groups, such as $-\text{N}(\text{CH}_3)_3^+$ that consists of quaternary group, $-\text{N}(\text{CH}_3)_3^+$ or $-\text{N}(\text{CH}_2\text{COOH})_2$, absorbed water which is a good solvent for such resins, the pore diameter become larger and larger (see Figs. 5—7). This is owing to the fact that the microspheres inside the resin beads possess a lot of strong polar group which hydrate strongly and cause the beads to expand considerably. Therefore, the pores in the microspheres become very large.

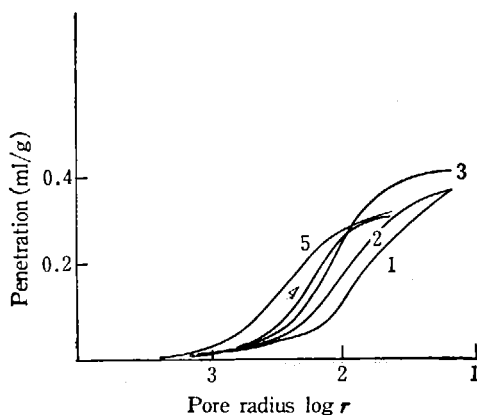


Fig. 5 Accumulative curves of pore volumes of resin containing $-\text{N}(\text{CH}_3)_3$, consisting of quaternary group
Water content (%): 1 0.0; 2 8.4; 3 11.9; 4 14.2; 5 20.0.

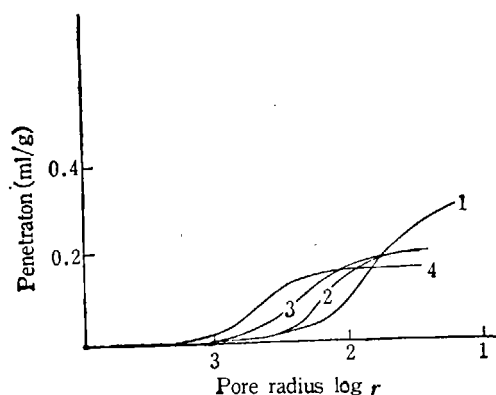


Fig. 6 Accumulative curves of pore volumes of resin containing $\text{—N(CH}_3\text{)}_3^+$ group
Water content (%): 1 0.0; 2 8.4; 3 16.4; 4 21.1.

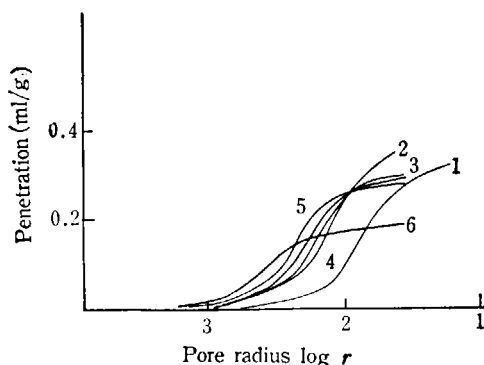


Fig. 7 Accumulative curves of resin pore volume containing $\text{—N(CH}_2\text{COOH)}_2$ group
Water content (%): 1 0.0; 2 5.5; 3 10.3; 4 15.8; 5 18.5; 6 27.7.

CONCLUSION

1. When the functional group is introduced into the copolymer of styrene-divinylbenzene, both the pore volume and radius are reduced and the surface area of most of the resins also reduced. However, for resins containing —NH_2 or —NHCH_3 group, the surface area increases evidently.
2. Ion exchange resins containing non-solvent possess larger pore volume and apparent volume than that in the dry state.
3. When the ion exchange resins absorb water, their average pore radii may increase up to 4–5 times as large as that of the dry resins.

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