The Sulfonation of Crosslinked Polystyrene Copolymerized with Polar Vinyl Compounds

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At present, most of strongly acidic cation-exchange resins are made by the sulfonation of crosslinked copolymers prepared from styrene and divinylbenzene. With a copolymer having a high degree of crosslinking, a long time is required for sulfonation because of its slow reaction rate. Although the reaction rate is increased by the addition of some catalyst[1] or solvent in order to swell the crosslinked copolymer,[2] no method has been reported to increase the rate of sulfonation by a modification of chemical composition of the crosslinked copolymer.

The present authors have found that the rate of sulfonation increases upon the introduction of small amounts of polar vinyl compounds, such as acrylonitrile, methyl acrylate and methylvinylketone, into crosslinked polystyrene as copolymerizable compounds.

Experimental

Copolymer beads (30—40 mesh) of styrene crosslinked with divinylbenzene (D. V. B.) were prepared by Pepper's method[3] in the presence of a 1.0% benzoyl peroxide initiator. In the copolymerization of styrene and D. V. B. with a polar vinyl monomer, some sodium chloride was added to the aqueous layer. The sulfonation of the crosslinked copolymer was carried out at different temperatures with a five-fold excess of 97.5% sulfuric acid under mechanical agitation.

To obtain a quantitative comparison of the sulfonation rate for each crosslinked copolymer, the increase in cation-exchange capacity was measured by the usual method,[4] this capacity was produced by the sulfonation of crosslinked polystyrene.

Results and Discussion

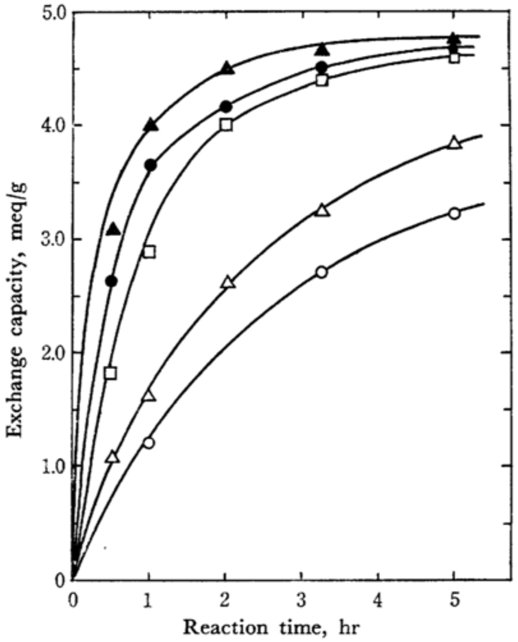

Fig. 1. Sulfonation of crosslinked polystyrene copolymerized with various vinyl compounds. (sulfonation temp. 110°C)
○ Homopolymer, copolymer with □ 1% AN, ● 1.7% MA, △ 2.0% MMA, ▲ 2.9% MVK

The crosslinked polystyrenes made by the copolymerization consisting of 92% of styrene, 8% (by weight) of D. V. B., and 0.02 mol% of acrylonitrile (AN), methyl acrylate (MA), methyl methacrylate (MMA) and methylvinylketone (MVK), were each sulfonated by sulfuric acid of a 36 normal solution at 110°C. The degree of sulfonation of these copolymers versus the reaction are shown in Fig. 1. These results indicate that the sulfonation rates of crosslinked polystyrenes made by the copolymerization of styrene, D. V. B., and polar vinyl compounds are much larger than that of styrene-D. V. B. copolymer, and that the use of acrylonitrile as the comonomer has a remarkable effect.

It has been described that, on the one hand, the rate of the sulfonation of crosslinked polystyrene is diffusion-controlled, since the reaction is entirely heterogeneous.[5] On the other hand, Reichenberg has reported that the difference in the sulfonation rates of crosslinked copolymers lies in the chemical rate, not in the diffusion.[6]

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1) N. E. Topp and K. W. Pepper, *J. Chem. Soc.*, **1949**, 3299.

2) R. M. Wheaton and D. F. Harrington, *Ind. Eng. Chem.*, **44**, 1796 (1952).

3) K. W. Pepper, *J. Appl. Chem.*, **1**, 124 (1951).

4) S. Fischer and R. Kunin, "Analytical Chemistry of Polymers," ed. by G. M. Kline, Interscience Publishers, New York, N. Y. (1959), p. 521.

5) E. E. Gilbert, "Sulfonation and Related Reactions," Interscience Publishers, New York (1965), p. 77.

6) G. D. Jones, "Chemical Reactions of Polymers," ed. by E. M. Fettes, Interscience Publishers, New York (1964), p. 282.

Recently, Wiley and Venkatachalam⁷⁾ have shown that, as kinetic evidence for diffusion control in the sulfonation of crosslinked polystyrene-bead copolymers, a plot of the square of the capacity against the time would be linear.

The results of the applications of Wiley's theory to the sulfonation of the crosslinked polystyrene copolymer with 1%, with 3%, and with 5% acrylonitrile at different temperatures did not show any linear relationships except in the case of a much higher reaction rate. When the sulfonation of crosslinked polystyrene is assumed to be a first-order reaction with respect to the polystyrene molecule, the following Eq. (1) is obtained:

$$Ps\frac{\mathrm{d}x}{\mathrm{d}t}=kPs(1-x) \qquad \ln\frac{1}{1-x}=kt \qquad (1)$$

where x is the degree of sulfonation, P represents the concentration of polystyrene (mol/l), and k is the rate constant.

Applying Eq. (1) to the sulfonation of the above-described copolymers, the linear slopes shown in Fig. 2 could be obtained.

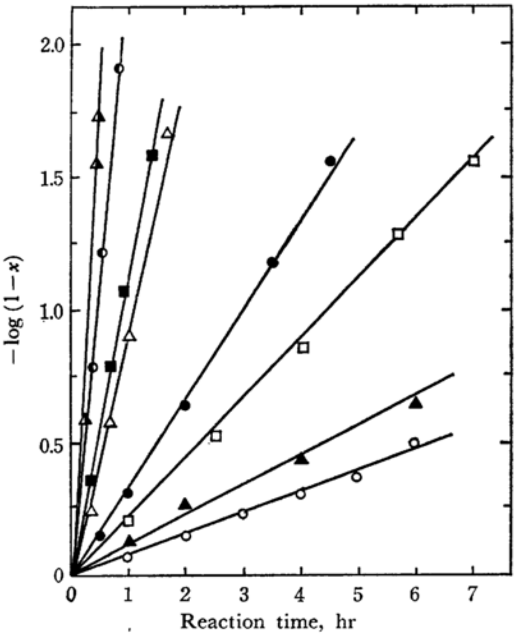

Fig. 2. First order plott of the sulfonation of crosslinked polystyrene copolymerized with acrylonitrile (AN).

	Copolymer with	Sulfonation temp., °C		Copolymer with	Sulfonation temp., °C
□	Homopolymer	110	◭	Homopolymer	130
○	1%	100	△	1%	120
●	3%	100	◐	3%	120
▲	5%	80	■	5%	100

In view of the above facts, it seems reasonable to assume, as in Reichenberg's description, that the sulfonation process of crosslinked polystyrene is controlled by the reaction rate itself, not by the diffusion rate.

The rate constants of the sulfonation reaction calculated from the linear slopes of Fig. 2 and the activation energy values obtained from the individual rate constants are given in Table 1. From the results, it may be seen that the activation energy for sulfonation decreases with an increase in the acrylonitrile content in the copolymer.

TABLE 1. RATE CONSTANT AND ACTIVATION ENERGY

AN(%)	Rate constant k (hr^{-1}) at different sulfonation temperatures, (°C)					Activation energy E, (kcal/mol)
	80	100	110	120	130	
0	—	—	0.466	—	8.01	43.6
1.0	—	0.174	—	2.38	—	38.1
3.0	—	0.678	—	6.48	—	32.9
5.0	0.308	2.93	—	—	—	29.5

This decrease in activation energy is considered to be caused by the neighboring-group effect of such a polar vinyl monomer as acrylonitrile copolymerized in crosslinked polystyrene; this is a characteristic feature of a chemical reaction on the polymer.

The rate constant of a sulfonation reaction using very small copolymer beads (80—100 mesh) consisting of 1% acrylonitrile by 97.5% sulfuric acid was observed to be k=2.84 hr^{-1} at 80°C. On the contrary, no reaction was observed when the same sized copolymer beads but without acrylonitrile were used under the same conditions.

This fact seems to indicate that the sulfonation in the crosslinked polystyrene containing polar vinyl compounds is increased, but the precise mechanism remains to be investigated in the future.

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7) R. H. Wiley and T. K. Venkatachalam, *Polymer Letters*, **4**, 981 (1966).