Anal. Calcd. for $C_{23}H_{21}BrO_2$: C, 67.5; H, 5.2. Found: C, 67.8; H, 5.1.

1-Bromo-1-phenyl-2-(m-methoxyphenyl)-2-(5-bromo-2-thienyl)ethylene (IX). The *ethylene* obtained from 2-(*m*-methoxybenzoyl)thiophene (15 g.) and benzylmagnesium chloride was a pale yellow, viscous oil (24 g.), b.p. 251–252°/20 mm.; treatment of this substance with 24 g. of bromine (in chloroform) yielded 25 g. of the *dibromo compound*, which crystallized from acetic acid in cream-colored needles, m.p. 94°.

Anal. Calcd. for $C_{19}H_{14}Br_2OS$: C, 50.7; H, 3.2. Found: C, 50.6; H, 3.1.

This compound was found to be identical with the monobromination product of the ethylene prepared from 5-bromo-2-(*m*-methoxybenzoyl)thiophene and benzylmagnesium chloride.

m-Fluorobenzophenone. To a solution of 30 g. of benzene and 12.5 g. of *m*-fluorobenzoyl chloride in 50 ml. of dry carbon disulfide, 15 g. of aluminum chloride was added in small portions with stirring, and the mixture left for 8 hrs. at room temperature, then refluxed for 1 hr. The usual treatment afforded 12 g. of *m-fluorobenzophenone*, which crystallized from ligroin as lustrous, colorless leaflets, m.p. 55°; the corresponding 2,4-dinitrophenylhydrazone crystallized from acetic acid in orange-yellow needles, m.p. 260°.

Anal. Calcd. for $C_{13}H_9FO$: C, 78.1; H, 4.5. Found: C, 77.9; H, 4.5.

o-Fluorobenzophenone. Similarly prepared from *o*-fluorobenzoyl chloride, this *ketone* is a pale yellow oil, b.p. 190°/29 mm., n_D^{22} 1.5898, which formed a 2,4-dinitrophenylhydrazone, m.p. 220°.

Anal. Calcd. for $C_{13}H_9FO$: C, 78.1; H, 4.5. Found: C, 77.8; H, 4.6.

The starting material for this synthesis, *o*-fluorobenzoyl chloride, was characterized by its condensation product with *p*-phenylenediamine in pyridine medium; *1,4-bis(o-fluorobenzoylamino)benzene* crystallized from acetic acid in shiny colorless prisms, m.p. 273°.

Anal. Calcd. for $C_{20}H_{14}F_2N_2O_2$: N, 8.0. Found: N, 7.9.

1,2-Diphenyl-2-(m-fluorophenyl)ethylene. Prepared from 10 g. of *m*-fluorobenzophenone and benzylmagnesium chloride (10 g.) in ether, this compound, b.p .229–230°/16 mm., n_D^{22} 1.6502, crystallized from ethanol in shiny colorless prisms, m.p. 55°; yield: 10 g.

Anal. Calcd. for $C_{20}H_{15}F$: C, 87.7; H, 5.5. Found: C, 87.6; H, 5.7.

1-Bromo-1,2-diphenyl-2-(m-fluorophenyl)ethylene (VII), prepared by treating 11 g. of the above ethylene with 6.4 g. of bromine in chloroform medium, crystallized from ethanol in shiny, colorless needles, m.p. 97°.

Anal. Calcd. for $C_{20}H_{14}BrF$: C, 68.1; H, 4.0. Found: C, 68.1; H, 4.3.

1,2-Diphenyl-2-(o-fluorophenyl)ethylene. This compound crystallized from ethanol as lustrous, colorless leaflets, m.p. 73°. Yield: 10 g.

Anal. Calcd. for $C_{20}H_{15}F$: C, 87.7; H, 5.5. Found: C, 88.0; H, 5.3.

Bromination of the foregoing compound yielded *1-bromo-1,2-diphenyl-2-(o-fluorophenyl)ethylene* (VI), which crystallized from ethanol in shiny, colorless prisms, m.p. 100°.

Anal. Calcd. for $C_{20}H_{14}BrF$: C, 68.1; H, 4.0. Found: C, 68.4; H, 4.0.

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[CONTRIBUTION FROM THE COLLEGE OF ENGINEERING, RUTGERS UNIVERSITY]

Matrix-Formed Adsorbing Polymers

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A method is described wherein the pore volume of dry silica gel particles is filled with a low viscosity, catalyzed epoxide prepolymer, this being subsequently polymerized. Following polymerization the siliceous matrix material is removed from the solid polymer by solution in aqueous hydrofluoric acid. The porous, resinous particles thus produced exhibited a capacity for adsorbing water vapor and for complexing copper, zinc, and hydrogen ion.

Conventional ion-exchanging polymers, in the usual particulate form, impose a permeability requirement on the polymer structure. This requirement, coupled with the needed inclusion of specific chemical groups for ion-exchange activity, has placed definite limitations on such compositions. The method described here provides an alternative route to securing the required permeability through casting of the polymer in a microcapillary form at the time of polymerization.

In the work described here silica gel particles were employed as a parent, matrix substance. Silica gel particles having a pore volume of 0.80 ml./g. were saturated with the required volume of the epoxide prepolymer, catalyzed with diethylene triamine. Following completion of the polymerization the silica gel matrix was removed by solution in a 27% hydrofluoric acid solution and washed thoroughly with distilled water. Detailed experimental procedure is given below.

The resinous particles thus prepared have been termed "gel replicas."

The water vapor adsorption measured for the material prepared above, and determined after drying the washed particles for two hours at 85–90° C., is given in Table I. A bulk polymerized material, of

TABLE I

WATER VAPOR ADSORPTION OF GEL-REPLICAS

Relative Humidity, 25°C., %	Adsorbed Water, gm. water/g. gel replica
100	0.48
81	0.26
51	0.069

corresponding composition, showed a water adsorption of only 0.007 gm./gm. polymer.

When the material was treated for a period of about 10 min. with a 5% sodium hydroxide solution, followed by washing with distilled water, ion-complexing of copper and zinc ions was observed, a preferential adsorption of the zinc ion being noted. The ratio of nitrogen atoms, derived from the amine, to metal-ion complexed, was calculated to be 3.8, thus corresponding approximately to the normal coordination number of 4.0. Adsorption of hydrogen ion was also observed.

As noted above, the weight of water vapor adsorbed by 1 g. of the gel replica, at saturation, was 0.48 gram. A calculation of this value was made independently, on a theoretical basis, from the concept that the void space in the resinous material corresponds to the solid space in the parent silica gel matrix. Taking the densities of the epoxide prepolymer, solid silica, and diethylene triamine as 1.23, 2.2, and 0.96 g./ml., respectively, gives a calculated value of 0.46 gram of water/g. of gel replica.

Similar gel replicas have been prepared using silica gel particles of spherical shape (bead form). Here the polymer particles obtained were of spherical shape and of density equal to 0.74 g./ml; the reduction below the density of the bulkpolymerized epoxide resin (1.16 g./ml), together with the water adsorptive values measured, is evidence of the porous structure of the gel replica particles.

This technique has been extended now to preparation of additional adsorbing polymers, and it is believed that the general method opens a new field in adsorption technology.

EXPERIMENTAL

Preparation of an epoxide-type gel replica. Diethylene triamine (5.7 g.) was added to 19.3 g. of a liquid, low-molecular weight epoxide prepolymer. Dried silica gel particles (24.8 g.) were then added to this solution and agitated for approximately 15 min. At the end of this period the initially liquid, organic phase was imbibed within the silica gel particles and a free-flowing mass of discrete solid particles obtained. These were heated at 100° for 1 hr. to complete the polymerization reaction, cooled to room temperature, and then placed in a 27% hydrofluoric acid solution. Within 20 min. the siliceous portion of the mass was dissolved, leaving an organic, particulate residue. These particles were thoroughly washed with distilled water and dried at 85°. This material was designated as "I" and exhibited the water adsorption properties shown above in Table I.

Hydrogen-ion adsorption of gel replica. A 5.00 g. portion of the material "I" was placed for approximately 5 min. in 200 ml. of 5% sodium hydroxide solution, washed with 200 ml. of distilled water, and then placed again for 5 min. in a fresh 200 ml. portion of 5% sodium hydroxide solution. Repeated washing with distilled water was then given until a *p*H of approximately 7.0 was obtained. This material was then dried for 1 hr. at 80–85°, and designated as II. Seven hundred seventeen thousandths gram of II was then added to 26.0 ml. of a 0.100*N* hydrochloric acid solution. The *p*H of this solution (glass electrode determination, 25°) before addition of the resinous particles, was 0.97. The *p*H was then followed as a function of elapsed time. This varied as indicated in Table II.

TABLE 2

Time, Min.	*p*H
0	0.97
5	2.10
10	2.40
15	2.65
30	3.20
60	3.75
90	3.95
120	4.20

Copper-ion complexing. A 0.507 g. sample of II was placed in a solution of 0.228 g. of $CuSO_4.5H_2O$ contained in 91 ml. of water. Decoloration of the copper sulfate solution was noted, and the originally colorless resinous particles assumed a pronounced blue color, indicating adsorption of the copper ion. Contact was allowed for 3 hr., with occasional agitation. The supernatant solution then showed 0.0097 gram of $CuSO_4.5H_2O$, corresponding to 0.218 gram adsorbed. A ratio of 3.86 gram-atoms of nitrogen/g.-ion copper adsorbed are calculated from these data and from the original polymer/amine composition.

Displacement of adsorbed copper ion by zinc ion. The pronounced blue coloration of the copper ion adsorbing gel replica particles noted above persisted visually unchanged after repeated washing with distilled water; when, however, the resinous particles, holding the adsorbed copper ion, were shaken with a 10 ml. portion of 0.30*N* zinc sulfate solution the blue color of the resinous particles disappeared, and the originally colorless zinc sulfate solution assumed a blue color, this indicating qualitatively a displacement of the copper ion.

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