

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 87, NUMBER 24

DECEMBER 23, 1965

Physical and Inorganic Chemistry

Oleophilic Ion-Exchange Polymers. I

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Oleophilic ion-exchange resins are ones capable of appreciable swelling in most organic solvents, and thus they have functional ion-exchange properties in these solvents. These resins were prepared by introduction into the polymer structure of hydrophobic or oleophilic groups which reduce the polarity of an ion-exchange polymer and make for its swelling in organic solvents. Oleophilic ion-exchange polymers were prepared by the copolymerization of methacrylic acid and dodecyl methacrylate; by the copolymerization of styrene and isobutylene, followed by sulfonation; by the formation of a cage polymer of polystyrene about a linear, oil-soluble polymer of isobutylene or butyl rubber, followed by cross linking (sometimes) and sulfonation; by the acylation (with lauroyl groups, as an example) of polystyrene, followed by sulfonation; by the quaternization with long-chain alkyl halides of polyvinylimidazole; by the chloromethylation of polystyrene, followed by treatment with a long-chain tertiary amine. In this manner, polymers were prepared which had appreciable swelling in a wide range of solvents varying from hexane or benzene on one hand to water on the other. The rates of exchange of certain of these oleophilic ion-exchange polymers in apolar solvents were shown to be comparable to those of conventional ion-exchange resins in aqueous media.

Introduction

Several attempts have been made in the past to extend the applicability of ion-exchange resins to non-aqueous solutions. In some solvents such as the lower alcohols, acetone, and aqueous solutions of alcohols, acetone, or dioxane, the use of conventional sulfonated

polystyrene resins (as an example) is practical although exchange rates are sometimes reduced. In the great majority of organic solvents, however, ion exchange with conventional resins is unsuccessful.

The principal difficulty in nonaqueous ion exchange arises because the resin matrix ordinarily does not swell sufficiently in the solvent to allow for an appreciable rate of the exchange process, which is almost invariably diffusion controlled. For example, in the reaction between a sulfonic acid resin and a base in organic solvents, reduced swelling severely reduces the rate.² This rate may even be negligible, which led some investigators to conclude that the capacity of the ion exchanger was different in different solvents.³⁻⁵ Other workers, notably Bodamer and Kunin⁶ and Watkins and Walton,⁷ found that resin capacities remained the same irrespective of swelling. This apparent discrepancy is caused by the fact that under conditions of hindered diffusion a pseudo-equilibrium⁸ can result and no noticeable change may occur in the system for long periods of time. Thus, even if the degree of swelling has no effect on the true capacity, it profoundly affects the feasibility of the ion-exchange process from a practical standpoint.

There have been two attempts to circumvent the low

(2) F. Helfferich, "Ion Exchange," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 516.

(3) T. Vermeulen and E. H. Huffman, *Ind. Eng. Chem.*, **45**, 1658 (1953).

(4) A. Gemant, "Ions in Hydrocarbons," Interscience Publishers, Inc., New York, N. Y., 1962.

(5) G. S. Panson and R. Ellsworth, *J. Org. Chem.*, **25**, 1466 (1960).

(6) G. W. Bodamer and R. Kunin, *Ind. Eng. Chem.*, **45**, 2577 (1953).

(7) S. R. Watkins and H. F. Walton, *Anal. Chim. Acta*, **24**, 334 (1961).

(8) G. S. Libinson, E. M. Savitskaya, and B. P. Bruns, *Proc. Acad. Sci. USSR, Chem. Sect.*, **145**, 133 (1962); *Dokl. Akad. Nauk SSSR*, **145**, 113 (1962).

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swelling of ion exchangers in nonpolar solvents. Water-wet resins were used in water-immiscible solvents.^{2,4,9} The rate of the ion-exchange process was thereby accelerated considerably. This method is a combination of liquid-liquid extraction and ion exchange, and its application is restricted to a limited number of solvents and solutes. Kunin¹⁰ and Millar¹¹ prepared macroporous resins. By employing appropriate diluents during the polymerization of styrene-divinylbenzene mixtures they obtained a highly cross-linked network containing a large number of sub-microscopic pores. The large internal surface and the relative rigidity of these structures permit rapid reactions between the resin and the solute in any solvent, but, because of the intrinsic density and non-swelling characteristics of their structures, the full capacity of these resins cannot be realized in nonpolar solvents. After 6 hr. Kunin obtained only about 60% neutralization of his macroporous sulfonate resin with triethylamine in solvents such as *n*-heptane and *n*-butyl alcohol.¹⁰

The approach that produces the most general solution of the problem is the enhancement of swelling by modification of the resin structure by the introduction of oleophilic groups which reduce the polarity of the resin structure and make for its swelling in solvents that do not solvate the sulfonate group, *i.e.*, most organic solvents. Cross-linked polystyrene does not truly fulfill this requirement since its swelling in aliphatic hydrocarbons is rather small¹² and it is difficult to effect a uniform, partial substitution of exchange groups in this resin. Polystyrene is quite convenient, however, with respect to the introduction of exchange groups, and this stiff backbone polymer has desirable mechanical properties. The modification of the structure of polystyrene to increase its swelling in hydrocarbons and other nonpolar solvents was therefore one of the principal aims of this study.

Experimental Section

Materials. Crude methacrylic acid (MA) (practical grade, Rohm and Haas) had a light orange color and was vacuum distilled to obtain a colorless product which crystallized at 15–16°. The dodecyl methacrylate (DMA) (faintly yellow, K and K Laboratories) was used as such. Styrene (Dow) was distilled *in vacuo* at 50° and stored at –10°. Commercial isobutylene, methyl chloride, and propane (Mallinckrodt) were used as such. The commercial divinylbenzene (DVB) (Koppers) contained 50–60% DVB, the remainder being largely ethylstyrene and diethylbenzene; the specific gravity of this mixture was 0.91. DVB was purified by extraction with base to remove the hydroquinone inhibitor; 5% sodium hydroxide was used in three extractions. Benzoyl peroxide (BzO₂), m.p. 102–103° (Matheson Coleman and Bell), was used. All monomers were kept under refrigeration until used.

Poly-*N*-vinylimidazole (PVI) was obtained from B.A.S.F. (Ludwigshaven, Germany) and was dried

in vacuo before use. Its average molecular weight was estimated to be 1.38×10^5 by light scattering.¹³ Its general properties and purity were described previously.^{14,15} Linear polystyrene (\bar{M}_n 145,000) (Foster Grant Co.) was purified by solution in methyl ethyl ketone and reprecipitation from methanol. Cross-linked polystyrene beads were: DVB 1, –50 + 100 mesh (Dow); DVB 1', –20 + 40 mesh (Rohm and Haas); DVB 2, –16 + 20 mesh (Pfaudler-Permutit); DVB 4, –100 + 200 mesh (Dow). The mole per cent DVB content is given as pure DVB. These were used without further purification. Chloromethylated polystyrene beads (DVB 8, about 50 mesh) were obtained through the courtesy of the Rohm and Haas Co. These were swelled in dichloroethane and stored at 5°; by analysis it was found that the resin was chloromethylated to 52% of theoretical.

Triethyl phosphate (TEP) (Eastman) was redistilled with the middle fraction boiling at 214–216° being used. Eastman White Label tributyl phosphate (TBP) (b.p. 154–157° (10 mm.)) was used as obtained. Tetramethylene sulfone (TMS) (Matheson) melted at 20–22° and was used as received, as was Fisher certified reagent grade 1,2-dichloroethane.

Stabilized liquid sulfur trioxide (Sulfan B, Baker and Adamson) and acetophenone (Fisher certified) were used without further purification. Chloromethyl ether (reagent grade, Matheson) was redistilled with the fraction boiling at 59.0–59.5° being used.

Lauroyl chloride was of reagent grade (Matheson) and was redistilled immediately before use, employing only the middle fraction boiling at 99–100° (1.5 mm.). Hexanoyl chloride (Matheson) was distilled under atmospheric pressure at 152.5–153.5°; stearoyl and acetyl chloride (Matheson) were used without further purification. When acylation procedure B was employed, the lauroyl chloride was used as received. The alkyl halides used were usually of Eastman White Label quality and were used as received. The tertiary amines used were of similar quality, except trimethylamine which was received as a 25% solution in methanol (Matheson). Aluminum chloride (reagent grade, Baker and Adamson) was used as received, as was analytical reagent grade anhydrous stannic chloride (Matheson).

Characterization Procedures. The exchange capacities of different resins were determined by the general procedures described by Gregor and Bregman.¹⁶ These procedures were modified for the examination of oleophilic resins. The capacities of the carboxylic resins were determined by shaking dry hydrogen form resin with an excess of 0.1 *M* sodium hydroxide (plus 1 *M* sodium chloride) in 50% (by volume) acetone-water for 1 day, followed by back-titration. Rate experiments showed that equilibrium was reached within a few hours. Water-ethanol solutions were used with the lauroylated-sulfonated resins. The capacities of anion-exchange polymers in the iodide state were determined by adding an excess of standard silver nitrate solution to a suspension of the resin and shaking to

(9) F. S. Chance, G. E. Boyd, and H. J. Garber, *Ind. Eng. Chem.*, **45**, 1671 (1953).

(10) R. Kunin, E. Meitzner, and N. Bortnick, *J. Am. Chem. Soc.*, **84**, 305 (1962).

(11) J. R. Millar, D. G. Smith, W. E. Marr, and T. R. E. Kressman, *J. Chem. Soc.*, 218 (1963).

(12) R. F. Boyer and R. S. Spencer, *J. Polymer Sci.*, **3**, 97 (1948).

(13) K. J. Liu and H. P. Gregor, *J. Phys. Chem.*, **69**, 1248 (1965).

(14) H. P. Gregor and D. H. Gold, *ibid.*, **61**, 1347 (1957).

(15) D. H. Gold and H. P. Gregor, *Z. physik. Chem. (Frankfurt)*, **15**, 93 (1958).

(16) H. P. Gregor and J. I. Bregman, *J. Am. Chem. Soc.*, **70**, 2370 (1948).

equilibrium, followed by back-titration. This was the customary procedure with the resins designated Im. The resins designated CA were placed in the chloride state and their capacities determined by displacement with sulfate, followed by a Mohr titration.

The accurate determination of the swelling of ion-exchange polymers was described by Gregor, *et al.*¹⁷⁻¹⁹; other variants of these procedures have also been described.² In this contribution, the solvent phase was removed by two somewhat different procedures. The first (A) was to shake a known weight of dry resin with excess swelling agent to equilibrium, then filter in a preweighed sintered glass crucible. Slow suction was employed to remove excess liquid from the resin but not allow it to dry. Results reproducible to better than $\pm 10\%$ were difficult to obtain by this simple method, but by adjusting the time of suction to the volatility of the solvent, one can achieve an accuracy which is estimated to be within $\pm 5\%$.

The second procedure (B) was to employ a coarse sintered glass crucible which could be centrifuged while inside a larger, enclosed tube at about 2500 r.p.m. for 3-5 min. A glass tube with one end stoppered with 100-mesh wire gauze supported by a Teflon ring served equally well. This procedure was reproducible to $\pm 1\%$ and of a high degree of accuracy.

The swelling of low cross-linked films of the anion-exchange polymers was determined by swelling to equilibrium and blotting to remove surface solvent, followed by weighing.

Swelling data are reported in terms of grams of imbibed solvent(s) per gram of dry resin, unless otherwise stated. The volume swelling ratio was calculated using the densities of dry resin and solvent, with the volume swelling ratio equal to the volume of sorbed solvent (assuming the sorbed solvent density was that of pure solvent) divided by that of the dry resin.

Routinely, polymers were dried *in vacuo* at 60° for 48 hr. to remove moisture and volatile solvents, unless otherwise stated.

Carboxylic Acid Resins. Carboxylic acid resins were prepared by the copolymerization of methacrylic acid and dodecyl methacrylate with a small amount of divinylbenzene added for cross linking. For the following discussion, the resins are assumed to be in the hydrogen state, unless otherwise stated.

A monomer mixture was prepared and nitrogen was bubbled through it for 5 min. immediately prior to use to remove oxygen. An appropriate 200-ml. flask in a constant temperature bath at 85° was used. First, 100 ml. of saturated sodium chloride was added to act as suspension medium and salt out the fairly soluble MA. Then nitrogen was bubbled through for 10 min. and the monomer mixture added with rapid stirring for 4 hr. under nitrogen. After 10 min., 1 g. of soluble starch in 10 ml. of saturated sodium chloride was added to act as suspension stabilizer and prevent clumping of beads. After 4 hr. the product was filtered on sintered glass and washed with water, then acetone, and then hexane. It was then dried *in vacuo*. Under

a microscope, the spherical particles were found to range in diameter from 0.1 to 0.3 mm.

Table I summarizes the composition and properties of these resins. The monomer mixture always contained 1% DVB (as pure DVB) and 2% BzO₂ (by weight). Yields were 83-90%, owing in part to the solubility of MA and incomplete recovery of very fine particles. The capacities of the resins were from 83 to 94% of that predicted from their compositions; the relatively high solubility of MA in water compared to DMA is probably responsible for the variation observed. Swelling equilibrium was reached rapidly, within 1 hr. to at least 90% equilibrium. Procedure A was employed for the swelling determination.

Table I. Properties of Oleophilic Carboxylic Resins

	MDI-1	MDI-2	MDI-3
MA/DMA, mole ratio	2	1	0.5
Swelling, g. of solvent/g. of dry resin			
Hexane	0.02	0.20	0.36
Benzene	0.47	1.23	1.11
Water	1.00	0.70	0.54
Acetone	1.53	1.25	0.66
Capacity, mequiv./g.	4.41	2.68	1.46
% theoretical	93.9	91.1	83.3

The data of Table I show, as anticipated, that the substitution of polar methacrylic groups by apolar dodecyl methacrylate groups increases the swelling of this polymer in hydrocarbon solvents and reduces its swelling in water, at the same degree of cross linking. As the apolar nature of the polymer is increased, its capacity must be necessarily lowered.

Sulfonated Styrene-Isobutylene Resins. Terpolymers of styrene, isobutylene, and DVB were prepared, then sulfonated to produce oleophilic cation-exchange resins. The same base polymer can be chloromethylated and then aminated to make the corresponding anion-exchange resin. The methyl chloride, isobutylene, and propane were liquefied as needed by passing the gas through a glass trap in a Dry Ice-acetone mixture. A 4% solution of aluminum chloride in ethyl chloride was prepared and stored dry at -10°, then diluted as used with methyl chloride or propane as a 0.5% solution. For one sequence of polymerizations, a mixture of styrene, DVB, isobutylene, and methyl chloride was made at -80° (measured with a thermocouple), and 60 ml. of 0.5% aluminum chloride in methyl chloride was added with vigorous stirring. The reaction was rapid, with evolution of methyl chloride and hydrogen chloride. The temperature then rose slowly to -30°. The polymer formed as a sticky mass. Then methanol was added to deactivate the catalyst and the resins were washed with acetone and dried *in vacuo*. Yields ranged from 30 to 60%. Resin IS-1 was prepared in a similar manner but employing propane. The catalyst also employed propane and the reaction temperature was -65°. Resin I-2 is the unsulfonated form of IS-2.

These resins were swelled prior to sulfonation; Wheaton and Harrington²⁰ have shown that this aids the physical stability of resins, and an earlier study by

(17) H. P. Gregor, K. M. Held, and J. Bellin, *Anal. Chem.*, **23**, 620 (1951).

(18) H. P. Gregor, F. Guttoff, and J. I. Bregman, *J. Colloid Sci.*, **6**, 245 (1951).

(19) H. P. Gregor, F. C. Collins, and M. Pope, *ibid.*, **6**, 304 (1951).

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

Feinland, Baldwin, and Gregor²¹ showed that pre-swelling was essential for sulfonation of copolymers having a relatively small fraction of benzene groups. The swelling agent employed was tetrachloroethylene (CHCl₂CHCl₂) and swelling equilibrium was attained within 15 min. Tetrachloroethylene (CCl₂CCl₂) was found to be equally suitable and without the toxic properties of the former. The swollen resin particles were treated for 8 hr. at 100° with concentrated sulfuric acid containing 0.2% silver sulfate as catalyst, then washed successively with acetone and water, and dried *in vacuo*. Each resin was Soxhlet extracted with hexane under reflux for several days, then redried for use.

A polymerization-alkylation from a mixture of styrene, DVB, and *t*-butyl chloride (9, 2.5, and 17 g., respectively) was also allowed to react and the product sulfonated, but its swelling in hexane was poor and its capacity was 3.7 mequiv./g., showing the resin was composed largely of styrene and DVB.

The oleophilic IS resins were somewhat rubbery in nature and irregular in shape. Table II summarizes their preparative procedures and properties. The density of resin I-2 was 0.76 in benzene and hexane and that of resin IS-2 was 1.00 in the same solvents.

Table II. Properties of Sulfonated Styrene-Isobutylene Copolymers^a

	Resin			
	IS-1	I-2	IS-2	IS-3
Monomer compn., g.				
Styrene	8.2	7.3	7.3	3.6
DVB	3.0	2.0	2.0	2.0
Isobutylene	21	28	28	28
Methyl chloride		35	35	35
Propane	40			
Swelling ^b				
Hexane	0.10	5.3	1.10	1.32
Benzene		6.4	1.21	
CCl ₄			3.60	
Dioxane	2.12	0.83	2.22	
Acetone		0.20		0.77
Water	3.05		0.97	0.86
Capacity, mequiv. g. ⁻¹	2.83		1.25	1.14
(Calcd.)	2.5		1.9	1.3

^a Resins in hydrogen form. ^b Swelling of Dowex 50-X2 is 0.03-0.04 in hexane and benzene, and 3.73 in water.

Table II shows that by the proper balance of hydrophobic and hydrophilic groups one can achieve approximately equal swelling in hexane and benzene on one hand and in water on the other (see resin IS-2). A later section in this paper will show that rates of exchange were comparable in all three solvents. In comparing the properties of these resins with oleophilic polymers prepared by side-chain substitution of acyl groups, it is seen that the position of substitution plays an important role but not a crucial one.

Sulfonic Acid Cage Polymers. Polymers were prepared by forming styrene-DVB cages about a linear, oil-soluble polymer. Polyisobutylene (PIB) is soluble in hydrocarbons such as hexane and was used as the linear material. It was shaken with a mixture of styrene

(21) R. Feinland, D. E. Baldwin, and H. P. Gregor, *J. Polymer Sci.*, 10, 447 (1953).

and DVB to form a gel, followed by polymerization. The polymerized product was then sulfonated to yield a cation-exchange resin.

Subsequently, Soxhlet extraction with hexane showed that almost 50% of their total weight could be leached from these polymers. To increase their stability, the cage mixtures were exposed to Co-60 γ radiation in an attempt to graft styrene onto the PIB chain.²² Also, butyl rubber, which is a copolymer of isobutylene and contains 1.5% isoprene, was used in place of PIB. It was assumed that styrene would react with the double bonds of the butyl rubber, forming bonds between the oil-soluble polymer and the cross-linked cage.

PIB was used as obtained from the Enjay Co. (Vistanex 80, $\bar{M} \cong 80,000$). A lower molecular weight product (10,000) was not suitable. The butyl rubber (Butyl) was used as obtained from Enjay (Butyl 217). The 10 g. of the rubber used (PIB or Butyl) was cut into 1-mm. pieces and placed in a flask to which was added a monomer mixture of styrene, DVB, and catalyst. The flask was shaken until a thick, homogeneous gel formed (approximately 4 days). All of the gels were then polymerized at 70° for 20 hr.

Sulfonation with concentrated sulfuric acid and 1% silver sulfate catalyst was found to be too vigorous, charring the resins. Therefore, the procedure of Turbak²³ which employs a complex of sulfur trioxide and TEP formed in various mole ratios was used.

The resins were dispersed in a blender and then swollen in 1,2-dichloroethane for 1 hr. prior to sulfonation. The complex was prepared by adding the appropriate amount of TEP to 50 ml. of dichloroethane, followed by the addition of sulfur trioxide dropwise. Room temperature was maintained by means of an ice bath while the complex was being formed. The complex was then added to the polymer with stirring. The products were added to water, washed free of sulfuric acid with water and acetone (barium nitrate test), washed with acetone, and dried *in vacuo*.

Exchange capacities were determined by direct titration of a weighed amount of the resin suspended in 1 *N* sodium chloride solution to the phenolphthalein end point; the titration usually required less than 30 min.

Table III lists the properties of the different cage resins prepared. The DVB contents of the monomer-polymer mixtures were 1-2%; BzO₂ was used as catalyst. The extracted material was essentially all found to be linear polymer. Resins prepared in a similar manner but without radiation lost all of their PIB upon prolonged extraction.

Other articles in this series will describe some of the ion-exchange properties of these cage polymers. Their fundamental properties are comparable to those of the other sulfonic acid polymers, but their physical properties were not as desirable for many uses.

Dodecylstyrene. In principle, a good starting point for the preparation of oleophilic ion-exchange polymers would be poly-*p*-dodecylstyrene. Overberger, *et*

(22) For a discussion of the effect of γ radiation on similar polymers, see A. A. Miller, E. J. Lawton, and J. S. Balwit, *ibid.*, 14, 503 (1954).

(23) A. F. Turbak, Preprints, paper presented before the Division of Polymer Chemistry, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961, Vol. 1, No. 2; see also A. F. Turbak, U. S. Patents 3,072,618 and 3,072,703 (Jan. 8, 1963).

Table III. Properties of Oleophilic Sulfonic Acid Cage Polymers

	Resins ^a				
	CSP-2 ^b	CSP-3 ^c	CSP-4 ^c	CSB-6 ^d	CSB-7
Styrene/PIB or -/Butyl, mole ratio	² / ₁₀	³ / ₁₀	² / ₁₀	³ / ₁₀	³ / ₁₀
Capacity, mequiv. g. ⁻¹	0.62	3.08	1.83	2.69	
% theoretical	23	89	70	75	
% extracted ^e		10		29	43

^a Resins designated P contain PIB; those designated B contain Butyl. ^b Polymerized, 1% additional DVB added, irradiated, and re-polymerized. ^c Exposed to 0.75 Mrep before polymerization. ^d Contained 3% DVB. ^e Three days Soxhlet extraction with hexane under reflux.

al.,^{24,25} prepared a series of *p*-alkylstyrenes through the *p*-acetyl-*n*-alkylbenzenes by Friedel-Crafts procedures, then reduced them with aluminum isopropoxide to the corresponding carbinols which were then dehydrated. In this study, a three-step modification of the earlier five-step procedure was developed, but with lower yields. Resins were not prepared because this procedure was not as practical as others. Briefly, *p*-(2-chloroethyl)phenyl undecyl ketone was prepared by the treatment of 2-chloroethylbenzene by a lauroyl chloride-aluminum chloride complex in dichloroethane to obtain the ketone in 48% yield, m.p. 29.5–30.5°.

Anal. Calcd. for C₂₀H₃₁OCl: C, 74.39; H, 9.68; Cl, 10.98. Found: C, 74.36; H, 10.08; Cl, 10.71.

This compound was reduced according to Clemmensen with amalgamated mossy zinc hydrogen chloride in xylene, with the final product, *p*-(2-chloroethyl)dodecylbenzene, being obtained by distillation at 185–190° (2 mm.) at a yield of 71%, and with a chloride content of 10.49%, compared to the calculated value of 11.48%. This product was converted to *p*-dodecylstyrene by refluxing with ethanolic potassium hydroxide followed by distillation to obtain the monomer at a yield of 8%, b.p. 165–173° (2 mm.).

Anal. Calcd. for C₂₀H₃₂: C, 88.16; H, 11.84. Found: C, 88.36; H, 11.53.

Acyl-Sulfonated Resins. Oleophilic sulfonic acid resins were prepared by the treatment of (cross-linked) polystyrene with a (long-chain) alkyl chloride, followed by sulfonation. An attempt to graft dodecyl groups onto a styrene-DVB resin using dodecyl chloride with an aluminum chloride catalyst in tetrachloroethylene at 35 and 85° led to little alkylation (less than 15%) at the former and extensive degradation at the latter temperature. The direct alkylation of cross-linked polystyrene with dodecyl chloride and anhydrous aluminum chloride at room temperature was too rigorous and a charred product resulted. The same reaction in cyclohexane led to a low (17%) degree of alkylation.

The acylation reactions were carried out in two different ways. In procedure A, 0.05 mole of linear polystyrene was dissolved in dichloroethane (5 g. in 75 ml.). An aluminum chloride-lauroyl chloride (1:1 mole) complex in dichloroethane (22 g., 13 g., and 100 ml., respectively) was prepared at room temperature and then added dropwise to the polymer solution under nitrogen. The reaction was carried out for 8 hr. at

(24) C. G. Overberger, C. Frazier, J. Mandelman, and H. F. Smith, *J. Am. Chem. Soc.*, **75**, 3326 (1953).

(25) C. G. Overberger, U. S. Patent 2,802,812 (1952).

54–58°, then poured into an excess of methanol. Precipitation was facilitated by the addition of 0.1% concentrated sulfuric acid. The polymer was washed with methanol and dried; the yield was 78% of theoretical.

Acylation procedure A was followed with cross-linked polystyrene beads except that these were swelled for a few hours in the solvent before the Friedel-Crafts reaction was carried out, and the beads were purified by extraction with methanol and then with acetone (Soxhlet) until no more aluminum could be detected by the ash test. An extraction with ether was also found to be effective in removing last traces of impurities. The use of chloroform in place of dichloroethane led to the same product.

Acylation procedure B allowed the beads to swell in a solution of lauroyl chloride in dichloroethane overnight, followed by the direct addition of aluminum chloride in powder form. For example, 382 g. of lauroyl chloride in 1.2 l. of dichloroethane was added to 100 g. of beads (DVB-1') at room temperature under nitrogen; the system was kept mildly agitated overnight. Then, 230 g. of aluminum chloride was added slowly, the temperature rising to 40°, where it was maintained for several hours. Then more solvent was added and decanted off; methanol was then added, followed by extraction with acetone-methanol-benzene mixtures. Yields by this procedure varied from 80 to 98%.

The acylated, linear polystyrene and cross-linked beads prepared by procedure A were sulfonated (Turbak²³), using the complex of sulfur trioxide and TEP formed in dichloroethane at 0°, with about 30 g. of the complex in 100 ml. of solution. The polymer was previously dissolved or swelled in 5–10 times its weight of solvent, and the sulfonation was carried out at 20° for 1 hr. The mixture was then poured into an excess of dichloroethane and filtered, and the product was washed with methanol, then water, and dried. The linear polymer became insoluble as the sulfonation proceeded; it was washed with solvent, dissolved in ethanol, reprecipitated with dichloroethane, and freeze-dried from water.

Sulfonation of acylated polystyrene prepared by procedure B was quite similar, with the complex being formed at about 35°, and the sulfonation reaction carried out at that temperature for 2 hr. For partial sulfonation, the acylated beads were swollen in dichloroethane; then TEP was added, followed by the addition of limited amount of Sulfan B. Under these conditions, only slight warming above room temperature was observed.

When toluene is subjected to a Friedel-Crafts acylation reaction, the acyl group goes almost exclusively to the *para* position.²⁶ Since this position offers the least steric hindrance with polystyrene, one can assume that substitution here was predominantly *para* with respect to the backbone. When a sample of lauroylated polystyrene (DVB-1') was extracted with boiling acetone, boiling benzene, and then with a boiling mixture of methanol-acetone-concentrated hydrochloric acid, it showed but an insignificant weight loss, indicative of its stability; the latter extracts were quite free of low-molecular-weight impurities.

The lauroylated-sulfonated resins were stable at room temperature and, when properly extracted, were

(26) H. Gilman and A. H. Blatt, *Org. Syn.*, **41**, 109 (1961).

Table IV. Preparation and Properties of Oleophilic Resins

No. ^a	Acylation method	%	Hexane swelling	SO ₃ /Ph	SO ₃ /TEP	Hexane swelling ^b	Capacity, mequiv./g.	Sulfonation, %
1'	B	0	<0.05	0.8	3	0.14 ^c	3.52	51
A1'	B	86	<0.05	0.8	3	0.14 ^c	1.44	23
Cl	A	96	...	4	3	0.03 ^d	1.71	54
L1'-1	A	42	...	5	3	<0.05 ^c	3.17	78
L1'-2	B	90	...	0.5	3	0.67 ^c	0.83	24
L1'-3	B	82	...	0.9	3	0.29 ^c	1.40	42
L1-4	A	90	1.32	2	2	0.22	1.14	39
L1-5	A	90	1.32	3	3	0.29	1.39	48
L1-6	A	94	...	4	3	0.40 ^d	0.99	36
L1'-7	B	98	1.27 ^c	5	3	0.06 ^c	2.57	84
L1-8	A	95	1.42	6	3	0.17	2.53	90
L1-9	A	98	...	7	3	0.16	2.00	69
L1-10	A	90	1.32	12	4	0.12	2.40	70
L1-11	A	96	1.32	13	7	0.07	2.79	100
L1-12	A	96	1.32	20	7	0.06	3.25	(2.8) ^e
L2-1	A	95	1.28	3	3	0.65	0.55	20
L2-2	A	85	1.38	6	3	0.15	2.42	82
S2	A	66	1.57	6	3	0.11	2.70	(2.2) ^e

^a A, acetyl; C, caproyl; L, lauroyl; S, stearoyl. ^b Swelling after sulfonation. ^c Swelling in heptane. ^d Swelling in cyclohexane. ^e Theoretical capacity.

Table V. Swelling of Acyl-Sulfonated Resins

Solvent	1'	S1'	A1'	AS1'	CS1	LS1'-1	LS1'-2	LS1'-3	LS1-6	L1'-7	LS1'-7	LS1-9
<i>n</i> -Heptane	<0.05	0.14	<0.05	0.14		<0.05	0.67	0.29		1.27	0.06	0.16
Diethyl ether	1.12	0.41	0.10	0.17		0.25	1.30	1.27		1.34	0.51	0.80
Cyclohexane	1.12	0.24	0.05	0.18	0.03	0.14	1.18	0.66	0.40	1.76	0.13	
Benzene	4.92	0.35	1.20	0.27	0.30	0.19	1.96	1.07	0.85	2.85	0.64	
Chloroform					1.15				2.21			
Acetone	0.84	1.42	1.16	0.72		1.37	1.36	1.82		0.41	1.75	1.55
1-Decanol	0.24	5.39	0.21	0.38		2.87	2.78	2.94		1.25	2.71	
Dichloroethane	4.80	0.62	4.73	1.67	0.57	0.30	2.33	1.35	0.98	4.18	0.94	
<i>n</i> -Pentyl alcohol						2.63					2.65	
Isopentyl alcohol						2.56					2.58	
Nitroethane					0.33				0.29			
Isobutyl alcohol						2.58					2.72	
<i>n</i> -Butyl alcohol	0.12	4.40	0.23	0.92		2.80	2.65	2.70	1.31	0.58	2.89	
<i>t</i> -Butyl alcohol						2.13					2.33	
<i>n</i> -Propyl alcohol						2.90					2.65	
Isopropyl alcohol						2.69					2.42	
Ethanol					1.29	2.95			1.15		2.66	
Methanol	0.12	6.23	0.24	0.60	1.75	3.16	1.53	2.41	0.98	<0.05	2.94	2.00
Water	<0.05	6.44	0.18	0.51	1.71	4.21	0.29	0.44	0.24	<0.05	0.83	0.52

quite free of analyzable low-molecular-weight impurities. When heated in the hydrogen form at 60° for 2 days they became dark, while at 105° in air for 3 hr. they became quite dark in color and showed an irreversibly reduced swelling in alcohols, as an example. In the salt form these resins are considerably more stable. Table IV summarizes the properties of the acyl-sulfonated resins, and Table V their swelling properties.

For Tables IV and V only a brief comment will be made here; subsequent papers in this series will present theoretical treatments of these oleophilic polymers. It suffices to point out that there is a regular sequence of properties in the polymers as the degree of acylation is increased and where the degree of sulfonation is varied. Possessing three rather different kinds of groups, namely aryl, alkyl, and polar (sulfonic acid groups), it is seen that different ratios of these groups produce resins of a wide and continuous range of variability. Table V shows that among isomers of the same alcohol there is a certain degree of specificity in the swelling of the same polymer. These resins are

characterized by excellent mechanical properties; they are firm beads, comparable in every way to the ordinary ion-exchange materials; their ion-exchange capacities are entirely practical, even for those polymers which swell as well in hexane as in water.

Attempts were made to carry out a Clemmensen reduction on linear, acylated polystyrene. An atypical result was observed in that reduction of the carbonyl to methylene resulted in cross linking, with the resulting polymer becoming insoluble in hexane and toluene, not melting, and containing a considerable amount of zinc even after exhaustive extraction with concentrated hydrochloric acid for 3 days. The same general results were obtained with cross-linked polystyrene. Other means of reducing the acyl group are under investigation.

In the Friedel-Crafts reaction, the time required to form the acyl chloride-aluminum chloride complex appears to be a function of the molecular weight of the acyl chloride. A long-chain compound such as lauroyl chloride does not react immediately with aluminum chloride, as is the case with acetyl chloride.²⁷ In this

work, either the complex was formed previously or it was formed *in situ* in the polymer. Both methods appear to be equally satisfactory with proper control of experimental conditions.

The acylation of polystyrene has been reported by Blanchette and Cotman,²⁸ who treated polystyrenes with butyryl and stearoyl chloride to obtain a 50 and 80% yield, respectively. The product became less soluble in benzene and methyl ethyl ketone as the length of the aliphatic substituent increased. The softening point of the polymers formed also decreased as the aliphatic chain was lengthened. Both of these general results were confirmed in our studies. Medalia, *et al.*,²⁹ treated polystyrene by means of a Friedel-Crafts alkylation reaction followed by saponification to form a polysoap. For example, polystyrene was treated with methyl undecylenate. Here the extent of alkylation was up to 50% for lower molecular weight polymers and that with a higher molecular weight polystyrene was about 36%.

A comparable sulfonation of acetophenone with an excess of a 3:1 sulfur trioxide-TBP complex at room temperature for 2 hr. was carried out. The reaction mixture was poured into water and the water layer separated. The acid was neutralized with sodium bicarbonate and sodium chloride was added to salt out the product which was collected at 0°. The crystals were washed with saturated salt solution and then ice water; the crystallization procedure was repeated, followed by drying the product *in vacuo*. The yield was 67%. For identification, the aniline salt was prepared and infrared analysis showed that sulfonation had occurred at the *meta* position to the ketone group. This salt melted sharply at 211.5–212.0°.

Anal. Calcd. for C₁₄H₁₅O₄NS: C, 57.30; H, 5.16; S, 10.92. Found: C, 57.43; H, 5.18; S, 11.26.

Thus, when carried out with comparable low molecular weight acyl compounds, sulfonation was complete and the carbonyl group was not affected. However, as shown in Table IV, more vigorous sulfonation apparently results in the detachment of the long chain and the preparation of a material with a high degree of sulfonation and a capacity higher than that obtainable without the degradation reaction.

It is of interest to compute the swelling of sulfonated resins in water on the basis of the moles of water sorbed per equivalent of sulfonic acid group present. From the data of Tables IV and V we see that swelling in water depends principally upon the position of the sulfonate group on the benzene ring. Sulfonated polystyrene S1' shows 102 moles of water sorbed per equivalent; the 42% lauroylated and 84% sulfonated resin LS1'-1, a value of 76; while the highly acylated (82–90%) resins with degrees of sulfonation varying from 25 to 98% (AS1', LS1'-2, LS1'-3, LS1'-7), values from 18 to 20. Thus, the sulfonate group in a *para* position produces strong sorption, while, when the *para* position is blocked by acylation and the sulfonate is probably in the *ortho* position, only about one-fifth as much water is sorbed by each sulfonic acid group.

(27) G. B. Baddelley, E. W. Wrench, and R. Williamson, *J. Chem. Soc.*, 2210 (1953).

(28) J. A. Blanchette and J. D. Cotman, Jr., *J. Org. Chem.*, 23, 1117 (1958).

(29) A. L. Medalia, H. A. Freedman, and S. Sinha, *J. Polymer Sci.*, 40, 15 (1959).

This is no doubt due to the considerable steric hindrance in the *ortho* position and the markedly lower polarity of this form. One might compare our results with those of Pepper³⁰ who sulfonated cross-linked (DVB 5) polystyrene and found 16 moles of water sorbed per equivalent of capacity over a wide range. There is considerable difference in the water-sorbing capacities of sulfonic resins of different degrees of cross linking. For example, Gregor, *et al.*,^{31,32} also found about 100 moles of water sorbed per equivalent of fully sulfonated polystyrene sulfonic acid of DVB 1, and about 25 moles for a DVB-5 resin (interpolated).

If each sulfonic group possesses a specific water-sorbing property, one could compute the water sorption by resin LS1'-1 as follows: This resin was 42% lauroylated and may be presumed to have 0.58 mole of *para*-sulfonated benzene rings which would sorb 59 moles of water. Since the total sulfonation is 0.78 mole, 0.20 mole of acyl-substituted groups would sorb 4 moles of water, for a total of 63 moles for 0.78 equivalent of sulfonic group or a capacity of 81 compared to the observed 76. This difference may be the result of error in the assumption that *all* unlauroylated residues are sulfonated, and *all* unsulfonated residues are lauroylated.

Quaternized PVI Polymers. Both linear and cross-linked PVI were treated to produce oleophilic polymers. The general procedures for quaternization followed those described earlier.¹³ The linear polymer was dissolved in the solvent (about one part in ten by weight) to which was added the alkylating agent. The system heated to reflux (65° for MeOH and 75° for TMS) and the polymer finally purified by dissolution and reprecipitation, followed by drying *in vacuo*. Table VI summarizes the results obtained. The molar ratio of PVI to alkylating agent was always 1:2. The yields are based entirely on weight for the linear polymers (no. Im-1 to -4), and for those formed by simultaneous quaternization and cross linking with 2% 1,5-diiodopentane (Im 2-1 and -2), while exchange capacities are determined for those resins previously cross linked (Im 7-1 to -6). Cross-linked PVI (Im 7-) was prepared by combining 0.4 mole of PVI and 0.032 mole of 1,5-diiodopentane in about 1 l. of methanol and heating at reflux for 2 days to obtain a soft gel. This was extracted with methanol (Soxhlet) for 3 days and then dried to obtain an 80% yield. This finely divided product (about 100 mesh) was then quaternized further as shown in Table VI.

The kinetics of quaternization reactions with polymeric amines have been studied by Fuoss, *et al.*,^{33–36} who have demonstrated that these do not conform to a simple bimolecular rate expression because of the effect due to the distribution of reacting sites. Repulsive forces are involved in the attachment of sites adjacent to those already quaternized, and consequently the

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

(31) H. P. Gregor, B. R. Sundheim, K. M. Held, and M. H. Waxman, *J. Colloid Sci.*, 7, 511 (1952).

(32) B. R. Sundheim, M. H. Waxman, and H. P. Gregor, *J. Phys. Chem.*, 57, 947 (1953).

(33) R. M. Fuoss, M. Watanabe, and B. D. Coleman, *J. Polymer Sci.*, 48, 5 (1960).

(34) B. D. Coleman and R. M. Fuoss, *J. Am. Chem. Soc.*, 77, 5472 (1955).

(35) P. L. Kronik and R. M. Fuoss, *ibid.*, 77, 6114 (1955).

(36) E. Hirsch and R. M., Fuoss, *ibid.*, 77, 6115 (1955).

Table VI. Properties of Quaternized Polyvinylimidazole

No.	Solvent	RX ^a	Time, days	Temp., °C.	Yield, %	Capacity, mequiv./g.		— Swelling in — solvents ^b							
						Calcd.	Measd.	A	B	C	D	E	F	G	H
Im-1	MeOH	C ₁₂ I	15	65	83		100%	0	3	3	0	0	2	s	s
Im-2	TMS	C ₁₂ I	1	80	66		92%	0	s	s	1	0	s	s	s
Im-3	TMS	C ₁₂ I	2	80	48			0	3	3	1	0	2	s	s
Im-4	TMS	C ₁₈ I	3	80	32			0	3	3	1	0	2	s	s
Im7-1	MeOH	Cl	3	65		4.24	3.58								
Im7-2	MeOH	C ₇ I	7	65		3.12	1.87								
Im7-3	TMS	C ₁₂ I	3	75		2.56	1.08								
Im7-4	TMS	C ₇ I	1	75		3.12	1.67								
Im7-5	MeOH	C ₇ H ₇ Cl ^c	7	65		4.55	1.98								
Im7-6	MeOH	C ₆ H ₁₁ Cl ^d	7	65		4.04	1.51								
Im2-1	TMS	C ₁₂ I	3	75	68										
Im2-2	TMS	C ₁₂ Br	3	75	62										

^a C₁₂I is dodecyl iodide, etc. ^b Swelling solvents are: A, methanol; B, benzene; C, toluene; D, ether; E, hexane; F, acetone; G, dioxane; H, chloroform. Swelling notation: 0, none; 1, slight; 2, moderate; 3, strong; s, soluble. ^c Benzyl chloride. ^d Phenethyl chloride

Table VII. Chloromethylated-Aminated Polystyrene-DVB 8^a

No.	Amine	Capacity, mequiv./g.	Amination from capacity, %	Swelling ^b		
				Hexane	Acetone	Water
CA8-1	(CH ₃) ₂ C ₁₂ H ₂₅ N	2.1	96	0.20	0.35	0.30
CA8-2	(CH ₃ CH ₂) ₂ C ₁₂ H ₂₅ N	1.7	69	0.10	0.49	0.58
CA8-3	(C ₇ H ₁₅) ₃ N	1.3	50	0.13	0.45	0.18
CA8-4	(CH ₃) ₃ N	3.2	100	0.05	0.20	1.38
CA8-5	(CH ₃) ₂ C ₆ H ₅ N	2.6	91	0.03	0.17	0.67

^a All resins in chloride form. ^b Swelling procedure B.

dielectric constant of the solvent employed plays a significant role. In this investigation a number of solvents of high dielectric constant were investigated, including methanol, propylene carbonate, nitroethene, and TMS. Of these, TMS with a dielectric constant of 42 at 50° and methanol with one of 33 at 25° gave most satisfactory results. As expected, the rate of quaternization decreased with increasing length of the alkyl substituent owing to both steric hindrance and the increasingly deactivating effects of methylene groups in this electrophilic reaction.

The solubility properties of the quaternized PVI polymers are most interesting. These might be compared to the quaternized polyvinylpyridines^{37,38} where there is a transition from polyelectrolyte to polysoap with increasing quaternization with long-chain alkyl halides.

The low extent of quaternization when treating cross-linked PVI is consistent with the observation of Fuoss, *et al.*,³³ because here the chain potential is particularly high.

Chloromethylated-Aminated Polystyrene. Chloromethylated DVB-1 polystyrene beads were prepared by swelling one part (by weight in grams) of beads in five (by volume in milliliters) of dichloroethane, and heating at 50° under nitrogen for 1 hr. with 1 vol. of chloromethyl ether. One part of chloromethyl ether was combined with 0.1 part of anhydrous stannic chloride (by volume) separately, and this solution added dropwise to the reactor, followed by continued heating for 80 min. The suspension was then poured into methanol containing 10% concentrated hydrochloric acid, fol-

lowed by prolonged washing in a 50% methanol-dioxane mixture and then drying *in vacuo*. The yield was 49% of theoretical.

These chloromethylated beads were then swollen in dioxane (13 g. in 100 ml.), 55 g. of N,N-dimethyldodecylamine was added, and the system was maintained at 35° for 2 days. The resin beads were then treated by a Kutscher-Steudel extraction apparatus for several days using methanol and then acetone to obtain resin CA1-1 in 96% yield. The same procedure using trimethylamine gave resin CA1-2 in 100% yield. Resins of the CA8 series were similarly aminated in methanol for 8 hr. under reflux, starting with the chloromethylated DVB 8 beads. Their properties are given in Table VII.

Anion-exchange films of a low degree of cross linking were prepared by dissolving 5 g. of polystyrene (mol. wt. 145,000) in 50 ml. of chloroform, adding a sixfold (molar) excess of chloromethyl ether containing 2% stannic chloride, pouring the solution into a large petrie dish, and allowing it to react for 1.5 hr. while covered at 50° under nitrogen (CA-1). This gelatinous film was washed with a methanol-dioxane mixture, swollen in 200 ml. of dioxane containing 21 g. of N,N-dimethyldodecylamine, and kept at room temperature for 4 days (CA-2). A similar procedure was followed using trimethylamine (CA-3).

Linear chloromethylated-aminated polymers were prepared by a modified procedure. With polystyrene of mol. wt. 10,000, 20 g. in 200 ml. of dichloroethane was treated with a complex of 75 ml. of chloromethyl ether and 2.5 ml. of stannic chloride at 50° for 30 min. The polymer was reprecipitated from methanol; then a suspension in methanol was treated with a twofold excess (molar) of N,N-dimethyldodecylamine in meth-

(37) H. E. Jorgensen and U. P. Strauss, *J. Phys. Chem.*, **65**, 1873 (1961).

(38) U. P. Strauss, N. J. Gershfeld, and E. H. Crook, *ibid.*, **60**, 577 (1956).

anol. After 5 hr. the polymer became soluble; the reaction was continued for 8 hr. more, and the polymer precipitated using hexane. Starting with polystyrene of mol. wt. 145,000, similar results were obtained. The reaction material of mol. wt. 10,000 was soluble in chloroform and ethanol, while that of higher molecular weight was insoluble in chloroform, swelling only in ethanol.

Chloromethylation with chloromethyl ether is advantageous because this is a good solvent for both polystyrene and chloromethylated polystyrene. It has been shown by several investigators, including Jones,³⁹ Pepper, *et al.*,⁴⁰ and Noda and Kagawa⁴¹ that during the chloromethylation of polystyrene, methylene bridges are derived from the chloromethylated derivative. Accordingly, the cross-linking reaction increases sharply as chloromethylation proceeds. The cross-linking reaction is, of course, reduced in extent by dilution.

The kinetics of the amination of chloromethylated polystyrene with trimethyl-, triethyl-, and tributylamines has been studied by Noda and Kagawa⁴¹ who found a second-order reaction, with the rate constant not changing over the entire reaction range. This finding agrees with our results, where amination was found to proceed rather independently of the molecular weight of the polymers, including those of low degrees of cross linking. Noda and Kagawa also studied the amination of benzyl chloride with a number of amines and found rate constants almost equal to the corresponding values with chloromethylated polystyrenes. The rates also decreased as the molecular weight of the amine increased. Accordingly, the decrease in amination with increasing chain length observed in this investigation would appear to be primarily due to steric hindrance, enhanced because of the high cross linking (DVB-8) of this polymer.

Rate Experiments. In a series of experiments, sulfonated styrene-isobutylene-DVB copolymers in the hydrogen state were treated with amines dissolved in different solvents. The IS resins were ground and screened; Dowex 50-X2 resin beads were also used. The rates of uptake or neutralization of diethylamine and of phenylethylamine were measured; the former is a fairly strong base ($pK_b = 3.22$). For each rate experiment, an amount of dry resin having a known capacity (about 0.5 mequiv.) was allowed to come to equilibrium with an excess of pure solvent, and then a known volume of the amine was added; the system was agitated vigorously and aliquots were withdrawn at different times. The concentrations of amines were either about 0.02 or 0.08 *M*, and did not decrease by more than 20% during the period from which rates were calculated because a substantial excess of amine was used. After equilibrium was reached, another aliquot was taken, and the uptake determined therefrom agreed well with the capacity of the resin. The aliquots in water were titrated directly with acid, using methyl red as indicator. Amines dissolved in hexane or benzene were extracted into an excess of standard, aqueous hydrochloric acid and the excess acid back-titrated as before.

(39) G. D. Jones, *Ind. Eng. Chem.*, **44**, 2686 (1952).

(40) K. W. Pepper, H. W. Paisley, and M. A. Young, *J. Chem. Soc.*, 4097 (1953).

(41) I. Noda and I. Kagawa, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **66**, 357 (1963); *Kogyo Kagaku Zasshi*, **66**, 857 (1963).

A plot of the amount of amine sorbed at time *t* divided by that sorbed at equilibrium (Q/Q_∞) gave a linear plot vs. $t^{1/2}$ when Q/Q_∞ was less than about 0.3. The rates of these processes are doubtlessly controlled largely by diffusion in the particle, with a simultaneous bimolecular chemical reaction occurring to form the salt, which in turn dissociates in a unimolecular process. The general theory of these systems has been discussed,⁴² but its rigorous application will require more accurate data than those obtained here. That particle-controlled diffusion is operative here can be shown by fitting the data to the plot for diffusion in a sphere (see Boyd, *et al.*,⁴³ and Gregor, *et al.*¹⁹), and one finds remarkably constant *B* values (proportional to $D^{1/2}$) for most of the data over almost the entire range of the process. One can estimate the diffusion coefficient of diethylamine in resin IS-2 in hexane, for example, to be about 3×10^{-6} cm.² sec.⁻¹, comparable to rates found for ordinary sulfonic acid resins in water.² By comparison, estimated diffusion coefficients in Dowex 50-X8 in hexane were 10^{-4} times those in the oleophilic resins. Dowex-50 resins varying in cross linking from 1 to 12% gave almost identical, slow sorption rates in hexane. The dependency of the initial rate upon particle diameter ($Q/Q_\infty \sim t^{1/2}/d$) also corroborates the supposition of particle-controlled diffusion. However, the solution concentration of amine is not proportional to the rate (except in water), suggesting that the amine rather than its ammonium form is the diffusing species in nonaqueous solvents. Table VIII summarizes the results of rate experiments.

Table VIII. Rate of Uptake of Diethylamine by Oleophilic Sulfonic Acid Resins

Solvent	Particle diameter, mm.	Amine concn., <i>M</i>	$t^{1/2}$, min.	$t^{-1/2}dQ/Q_\infty \times 10^{-8}$
Resin IS-2				
Hexane	0.90	0.018	0.65	7.2
Hexane	0.90	0.073	0.30	10
Benzene	0.87	0.018	1.0	5.2
Benzene	0.87	0.077	0.25	11
Benzene	1.4	0.018	2.0	9.6
Water	0.81	0.018	0.60	6.5
Water	0.81	0.073	0.08	16
Hexane ^a	0.90	0.020	1.1	6.3
Hexane ^a	0.90	0.082	0.23	9.9
Resin IS-1				
Hexane	0.68	0.018	2.0	3.4
Hexane	0.68	0.075	2.0	3.4
Water	1.04	0.018	0.30	13
	1.04	0.074	0.08	25
Resin Dowex 50-X8				
Hexane	0.21	0.018	400 ^b	0.0004

^a Phenylethylamine. ^b Extrapolated from initial rate.

The following papers in this series will present a statistical mechanical treatment of the swelling of the lauroylated polystyrene polymers and a discussion of the swelling of these and their sulfonated analogs in different solvents.⁴⁴ The uptake of mixed solvents by the chloromethylated-aminated anion-exchange polymers has also been studied and treated from a theoretical

(42) J. Crank, "Mathematics of Diffusion," Clarendon Press, Oxford, 1956.

(43) G. E. Boyd, A. W. Adamson, and L. S. Myers, *J. Am. Chem. Soc.*, **69**, 2836 (1947).

(44) A. G. Tsuk and H. P. Gregor, *ibid.*, **87**, 5534 (1965).

point of view.⁴⁵ The phase equilibria with different bases and the acyl-sulfonated ion-exchange polymers have been investigated, and a number of chromatographic separations involving a number of different amines, including alkaloids of biological origin, will be described.⁴⁶ Cation-exchange processes involving sulfonic acid polymers and metal chelate complexes dissolved in nonaqueous solvents were also investigated.

(45) M. Shida and H. P. Gregor, *J. Polymer Sci.*, in press.

(46) A. G. Tsuk and H. P. Gregor, *J. Am. Chem. Soc.*, 87, 5538 (1965).

Acknowledgments. The authors wish to thank the sponsors who supported a part of the work on the preparation of these oleophilic polymers and later on their characterization: Vanadium Corporation of America (Ph. T. and M. S.); Office of Naval Research (G. K. H.); the United States Public Health Service (A. G. T. and M. S.). Parts of this report were abstracted from the dissertations of M. Shida (June 1964) and A. G. Tsuk (June 1964), and from the B.S. thesis of J. Potenza (June 1962), submitted to the Polytechnic Institute of Brooklyn, N. Y.

Oleophilic Ion-Exchange Polymers. II. Swelling of Cross-Linked Networks with Multiple Hetero Side Chains

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The theory of swelling of a cross-linked network with a large number of flexible side chains of a different kind (heterograft) was developed along the lines of Flory's statistical-mechanical treatment. The partial molar free energy of mixing of the multibranched polymer with solvent is

$$\frac{\Delta G_1}{RT} = \ln(1 - v_2) + v_2 + \frac{X_\beta + gX_\sigma}{1 + g} v_2^2 + \frac{V_1 v_e}{Q_\beta} \left[\left(\frac{v_2}{1 + g} \right)^{1/3} - \frac{1}{2} \left(\frac{v_2}{1 + g} \right) \right]$$

where the subscript β refers to the backbone and σ to side chains, g is the volume ratio of side chains to backbone, Q_β is the total volume of the unbranched polymer, and other symbols have the same meaning as in Flory's derivation. Upon subtracting from this expression the partial molar free energy of mixing of the unbranched polymer with solvent, $(\Delta G_1/RT)$, we obtained the difference Δ due to the introduction of side chains

$$\Delta = \frac{g}{1 + g} (X_\sigma - X_\beta) v_2^2 - \frac{V_1 v_e}{Q_\beta} \left[v_2^{1/3} - \left(\frac{v_2}{1 + g} \right)^{1/3} - \frac{v_2 g}{2(1 + g)} \right]$$

If, at the v_2 value corresponding to maximum swelling of the unbranched network $\Delta < 0$, then the introduction of side chains will increase swelling. If $\Delta > 0$, a decrease in swelling will result. By neglecting the numerically small second term in the Δ expression, and by expressing X in terms of cohesive energy densities, the arithmetic mean of the cohesive energy densities of the backbone and side chains emerges as a dividing line. For lauroylated polystyrene this value was $8.5 \text{ (cal. ml.}^{-1}\text{)}^{1/2}$, and theory predicts that swelling of polystyrene will be increased by the introduction of lauroyl side chains for all

solvents whose cohesive energy density (δ_1) is lower than 8.5, and decreased for solvents with $\delta_1 > 8.5$. Measurements of the swelling of lauroylated polystyrene largely confirmed these predictions. The introduction of polar (acetate or sulfonate) groups into polystyrene or lauroylated polystyrene reduced swelling in nonpolar solvents. Lauroylated and partially sulfonated cross-linked polystyrene was found to swell considerably in a number of solvents tested, including hydrocarbons.

The problem in extending the use of ion-exchange resins towards nonaqueous solvents, especially hydrocarbons, arises primarily because of the insufficient swelling of ordinary ion exchangers in these solvents. Several attempts were made in this laboratory to increase the swelling of ion exchangers in nonpolar solvents by chemical modification of the resin matrix. The results of this work are given in the accompanying paper.² Among the most promising of these modifications was the grafting of lauroyl side chains onto cross-linked polystyrene by means of a Friedel-Crafts condensation. The resulting resin was then sulfonated to give a cation exchanger.

This paper reports the changes in swelling in various solvents that occur when flexible side chains and/or polar groups are introduced into cross-linked and sulfonated polystyrene, and correlates these changes with the thermodynamic theory of swelling.

Theoretical

Flory³ has developed a theory for the swelling of cross-linked polymer networks. Our derivation of the free energy of mixing for lauroylated polystyrene is analogous to Flory's, except that the flexibility of the multiple side chains as well as the chemical dissimilarity between

(1) Taken from the dissertation submitted to the faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1964.

(2) H. P. Gregor, *et al.*, *J. Am. Chem. Soc.*, 87, 5525 (1965).

(3) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.