# Polymer Swelling 2: A Restudy of Poly(Styrene-co-Divinylbenzene) Swelling in Terms of the Cross-link Density<sup>1</sup>

L. A. ERREDE, 3M Science Research Laboratories of Central Research, 3M Center, Bldg. 201-2N-22, St. Paul, Minnesota 55144

## **Synopsis**

A very convenient and reliable gravimetric method was developed for measuring swelling of poly (styrene-co-divinylbenzene) in particulate form. The method is based on the gravimetric procedure reported earlier<sup>2</sup> for monitoring liquid uptake by thin (<0.3 mm) microporous composite films, consisting of swellable particulate (80% by weight) enmeshed in poly(tetrafluoroethylene) microfibers (20%). The swellability S (in milliliter of liquid absorbed per gram of polymer in equilibrium with excess liquid) for six sty-co-DVB polymers with crosslink densities  $\varrho$  ranging from 0.01 to 0.12 was measured in 19 organic liquids. In each study of S as a function of  $\varrho$  the relationship was given by

$$S = C(\varrho - \frac{1}{3} - \varrho_0^{1/3}) = C(\lambda^{1/3} - \lambda_0^{1/3})$$

where  $\lambda = 1/\rho$  is the average number of carbon atoms in the "backbone" of the polystyrene segments between cross-link junctions, C is the relative swelling power of the liquid, and  $\rho = 1/\lambda_0$  is the critical cross-link density above which S is equal to zero.

# INTRODUCTION

It is well known<sup>3-5</sup> that determination of polymer swellability was, and still is, a very time-consuming procedure that often yields results of only limited reliability, owing primarily to the ill-defined dimensions and/or inability to measure accurately the weight of the gelled polymer sample at equilibrium swelling in excess liquid. The early investigators of poly(styrene-co-divinylbenzene) swelling<sup>3,4</sup> waited 3–7 days for copolymer samples to equilibrate with solvent before removing the sample for dampdrying between absorbent materials and subsequent measurement of liquid uptake, either gravimetrically or volumetrically. The reproducibility of the measured volume and/or weight of the damp-dried gelled polymer samples was poor at best, and consequently as much as 40 replicate determinations were averaged together to obtain one reliable value<sup>4</sup> for the swelling ratio  $(V_g - V_p)/V_p$ , where  $V_g$  and  $V_p$  are the volumes of the polymer in the gelled and dry states, respectively.

The precision in measuring  $V_g$  and  $V_p$  has been much improved by modern investigators,<sup>6</sup> who utilize sophisticated electronic and/or photographic equipment to determine the volume of the polymer in the form of spherical microbeads before and after swelling in the test liquid. These measurements are made either on a single microbead<sup>7</sup> or on a statistical sampling,<sup>8</sup> the distribution (Fig. 1a and b) of which is well characterized before and after



Fig. 1. SEM photomicrographs of a microporous composite sheet consisting of Biobeads SX-8 (a) and (b) enmeshed in PTFE (20.2%; Table 1). (c) Top surface of the composite sheet viewed at a 45° angle from the horizontal. (d) Freeze-fractured edge of the 0.25-mm thick sheet viewed at a 0° angle from the horizontal plane.

swelling. Although these measurements are considerably more precise than those of the early investigators, they are nonetheless time consuming and they require very expensive instrumentation.

The good reproducibility of results obtained in our study of liquid uptake by microporous composite films<sup>2</sup> consisting of cross-linked polymer (> 80% by weight) enmeshed in poly(tetrafluoroethylene) microfibers (< 20%, Fig. 1c and d) encouraged us to investigate the possibility that these composite films might be ideally suited for the measurement of liquid uptake by crosslinked polymers at gelled equilibrium saturation in excess liquid. Even when swelled 93-fold (Fig. 2 of Ref. 2), these microporous composite films are tough enough to be handled like normal continuous films of good physical integrity. The interlaced network of inert PTFE-microfibers in the composite film provides the binding force that resists tension in the gelled state and permits the composite film to be damp-dried reproducibly by surface contact between multiple sheets of soft absorbent paper. It also enables the composite films to be handled roughly without fear of measurable loss of entrapped particles, even after 100 cycles of swelling to equilibrium and redrying. The open-celled structure (Fig. 1c and d) allows easy access of



Fig. 2. Volume S (mL) of benzene absorbed per gram of poly (sty-co-DVB) at equilibrium swelling as functions of (a) cross-link density q, (b)  $q^{-1}$ , (c)  $\rho^{-1/2}$ , and (d) $q^{-1/3}$ .

fluids to the particulates, which undergo rapid swelling to saturate equilibrium in excess liquid. Our time studies of liquid uptake by such thin (<0.3 mm) microporous (>0.4 porosity) composite films showed that the void space of the sample was filled by capillary action within the first few minutes after surface contact with the test liquid and that swelling of the entrapped particulates to the equilibrium state occurred within 0.5-2 h thereafter, depending primarily upon the surface-to-volume ratio of the particulate. Although comminution of the copolymer to a fine powder and subsequent conversion to a microporous membrane, as described in the Experimental section, is somewhat time consuming, this disadvantage is more than compensated for by the advantage that the composite microporous film made thereby can be used repeatedly in subsequent swelling-drying cycles using the same or different liquids, which eliminates errors attributable to sampling and geometry.

This paper describes how the above procedure, which was designed originally to give S' in milliliters of liquid absorbed per gram of *composite*, was modified to yield S in milliliters of liquid absorbed per gram of *polymer* contained in the composite film, and it also reports the results obtained using the modified procedure to study swelling of poly(styrene-co-divinylbenzene) as a function of cross-link density.

## **EXPERIMENTAL**

# **Preparation of Microporous Composite Films**

Samples of poly(styrene-co-divinylbenzene) in the form of microbeads were purchased from Bio-Rad Laboratories, Bio-Beads SX-1, SX-2, SX-3, SX-4, SX-8, and SX-12. The DVB mole fraction r (Table I) in each of these samples was determined by Bio-Rad Laboratory personnel<sup>9</sup> on the basis of the corresponding molar ratios of diethylbenzene to ethylbenzene obtained via thermal degradation of representative samples. Aliquots of each poly(Sty-co-DVB) sample were converted by us into the corresponding microporous film (Fig. 1) consisting of the Bio-Beads (>80%) enmeshed in PTFE microfibers (< 20%), as described in detail elsewhere.<sup>2</sup> Briefly, this procedure utilized a rubber mill to convert a watery mixture of the Bio-Beads (20 g), water (10 mL), and Teflon 30-B aqueous emulsion (8 mL; 60% PTFE and 8% wetting agent) into tough films each about 400 cm<sup>2</sup> in area and about 0.25  $\pm$  0.02 mm thick. At the end of this work-intensive procedure, the composite film consists of the particulate enmeshed in PTFE in a continuum of soapy water. The soap solution was removed by diffusion and elution overnight in a slow stream of warm water. The water-saturated composite films were damp-dried between multiple sheets of absorbent paper and then weighed to the nearest tenth of a milligram. The films were allowed to dry overnight at ambient room conditions and then for an additional hour in vacuum at 100°C. The dry films were reweighed to the nearest tenth of a milligram to determine by weight difference the volume of water in the film prior to drying. This volume  $V_0^{w}$  in milliliters of water per gram of composite, represents the volume occupied formerly by water at the end point of the procedure for film fabrication, which after drying

Film sample no.ª	SX-1	SX-2	SX-3	SX-4	SX-8	SX-12
1	0.010	0.023	0.034	0.042	0.080	0.119
p-1/3	4.66	3.54	3.12	2.91	2.38	2.11
TS	$370\pm55$	$250\pm40$	$430 \pm 50$	$530\pm75$	$370\pm 65$	$450\pm35$
V <sup>w</sup>	$0.70\pm0.12$	$0.82\pm0.12$	$0.65\pm0.10$	$0.62 \pm 0.12$	$0.72\pm0.05$	$0.65 \pm 0.10$
Ň	$0.68\pm0.16$	$0.75\pm0.06$	$0.65\pm0.09$	$0.70 \pm 0.12$	$0.75\pm0.12$	$0.69 \pm 0.10$
W <sub>0</sub>	0.623	0.935	1.246	1.558	1.869	2.181
x	0.801	0.799	0.803	0.796	0.798	0.804
$V_0$	0.43	0.73	0.81	1.03	1.36	1.46
<sup>a</sup> Film	sample number	corresponds witl	h Bio-Rad Labora	atories Bio-Beads	number for the	poly(Sty-co-DVB)

sample that was used to make the corresponding film.

r, molar ratio DVB in the Sty-Co-DBV polymer, which was determined pyrolytically by Bio-Rad Laboratories. p, cross-link density = r/(1 + r).

TS, tensile strength, in psi; average of three samples.  $V_0^{\mu}$ , water of film composition before evaporation to dryness (in mL/g of composite) (average of five film samples).

 $\mathbf{V}_{0}^{0}$ , volume of wetting but nonswelling liquid absorbed by capillary action (in ml/g of composite); average of eight liquids: hexane, heptane, hexadecane, methanol, ethanol, *n*-propanol, *n*-butanol, and *n*-hexanol.

 $W_0$ , weight of composite film sample used for swelling study.

x, weight fraction of poly(Sty-co-DBV) contained in  $W_0$ .  $V_0$ , void volume contained in  $W_0$ ; that is,  $V_0 = W_0 V_0^0$ 

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is void volume that can be refilled with an organic liquid by capillary action.

These microporous composite film samples were extracted further by swelling to equilibrium in acetone, toluene, and again in acetone to ensure removal of extraneous solubles, including residual soap. Samples of the extracted films were submitted for carbon, hydrogen, and fluorine analyses, the sums of which were 99.6  $\pm$  0.6%. Thus, the elementary analysis was considered reliable enough to permit calculation of the corresponding weight fraction of PTFE (1 - x), and by difference the weight fraction x (Table I), of the Sty-co-DVB polymer in the composite film.

An aliquot swatch was cut from each of the six composite films. The size of the switch was related inversely to the cross-link density of the particulate polymer used to make the composite film. This order in relative area of sample was selected to compensate for the expected decrease in absorption capacity per gram of polymer as a function of cross-link density of that polymer. The samples were labeled with indelible markings (India ink or very soft lead pencil) to correspond with the SX designation of the Bio-Beads (Table I). The set of six swatches, one from each of the six films, was immersed in a given test liquid, and the uptake thereof by each of the six swatches was monitored simultaneously as a function of time as described previously.<sup>2</sup>

# Studies of Liquid Uptake as a Function of Cross-link Density

The swatch cut from the composite film made from Bio-Beads SX-1 was placed on the surface of the test liquid contained in a 9-cm diameter petri dish. When absorption by capillary action from the bottom to the top surface was complete, as evidenced by uniform wetting across the top surface, the next swatch cut from the composite film made from Bio-Beads SX-2 (Table I) was laid on top of the first, and so on until all six swatches in the order of increasing cross-link density were stacked one on top of the other in enough added liquid to cover generously the top surface of the sixth swatch, SX-12. Time studies (Fig. 7 of Ref. 2) of liquid uptake by microporous composite films of this ilk had shown that equilibrium was virtually established within 30 min. Nevertheless, the six swatches were allowed to remain in the test liquid overnight to ensure true equilibrium before measuring gravimetrically the magnitude of liquid absorbed by each swatch. This was carried out as follows: The stack of six swatches was inverted so that sample SX-1 could be removed first. It was damp-dried between multiple sheets of soft absorbent paper. The damp-dried sample was weighed to the nearest tenth of a milligram in a capped weighing bottle to preclude loss of liquid by evaporation. After all six swatches were weighed, the absorbed test liquid was leached out from each of the six swatches by liquid exchange with 1 L acetone for 1 h, followed by further liquid exchange for an additional hour in a fresh liter of acetone to ensure removal of trace amounts of test liquid. The samples were again damp-dried between multiple sheets of soft absorbent paper and then allowed to dry at room temperature under a gentle stream of warm air, followed by an additional hour of drying in vacuum at 100°C. The samples were again weighed to the nearest 0.1 mg to ensure that removal of the last traces of the previous test liquids was complete before reswelling the set of six swatches in the next test liquid.

The volume S in milliliters of liquid absorbed per gram of Sty-co-DVB polymer, was calculated by means of the equation

$$S = \frac{[(W_s - W_0)/d - V_0]}{xW_0}$$

where  $W_s$  and  $W_0$  are the respective weights of the swatch saturated with test liquid and subsequently redried, d is the density of the test liquid,  $V_0$ is the void volume of the swatch, and x is the weight fraction of poly(Styco-DVB) in the swatch. The observed S was plotted as a function of the corresponding cube root of the inverse of cross-link density  $\rho$  to obtain the characteristic straight line (see Fig. 4) given by

$$S = C(\varphi^{1/3} - \varphi_0^{1/3})$$

where C is the relative swelling power of the liquid and  $\rho_0$  is the critical cross-link density of the polymer at or above which S = 0. The constants C and corresponding  $\varphi_0^{-1/3}$  determined for 19 test liquids are collected in Table II.

# **RESULTS AND DISCUSSION**

# **Determination of Swellability of Sty-co-DVB Polymers**

In our previous study we measured  $V_s$ , the total volume of liquid absorbed by the poly(Sty-co-DVB) enmeshed in PTFE composite film to obtain S', in milliliters of liquid absorbed per gram of microporous composite film at saturation equilibrium with excess liquid. In this study, however, it is necessary to measure  $\Delta V = V_s - V_0$ , the volume of liquid absorbed by the

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Liquid	BP (°C)	Density	С	$\rho_0^{-\nu_3} = \lambda_0^{-\nu_3}$
N,N,-dimethylaniline	193	0.9819	2.25	1.80
Cyclohexanone	157	0.9478	2.16	2.05
Anisole	154	0.9961	2.00	1.70
Benzene	80°	0.8787	2.14	1.70
Toluene	111	0.8669	2.02	1.75
1,4-Dibromo- <i>n</i> -butane	(63 at 6 mm)	1.808	1.82	1.85
1,4-Dichloro- <i>n</i> -butane	161	1.16	1.78	1.70
<i>n</i> -Butyl bromide	102	1.2758	1.73	1.66
<i>n</i> -Butyl iodide	130	1.615	1.69	1.95
Pyridine	115	0.9819	1.63	1.72
Methyl-n-butyl ketone	127	0.828	1.50	1.80
<i>n</i> -Butyl chloride	78	0.8862	1.40	1.70
<i>n</i> -Butyl acetate	126	0.8825	1.33	1.60
cis-Decahydronaphthalene	193	0.7785	1.00	1.85
trans-Decahydronaphthalene	185	0.8699	0.80	1.80
(Trifluoromethyl)benzene	102	1.1884	0.71	1.85
Cyclohexane	81	0.7785	0.53	1.95
<i>n</i> -Butyl ether	142	0.764	0.51	1.50
n-Butyl alcohol	118	0.81	0	

TABLE II Swelling Parameters C and  $\rho_0^{-\nu_0}$  for Various Liquids

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poly(Sty-co-DVB) component per se to obtain S, in milliliters of liquid absorbed per gram of poly(Sty-co-DVB), at saturation equilibrium with excess liquid. To obtain the latter, it is necessary to know  $V_0$ , the volume of liquid required to refill the void space of the microporous film, so that it can be subtracted from  $V_s$  to give  $\Delta V$ , which is then divided by the dry weight of copolymer in the composite sample; that is,  $w = xW_0$ , where x is the weight fraction of copolymer in the composite film and  $W_0$  is the dry weight of the composite film used to absorb the test liquid.

When these composite films are made as described in the Experimental section, they are in effect liquid-supported membranes, that is, saturated with water. When these films are subsequently dried, they become microporous; the volume space occupied formerly by water is now the void space  $V_0$ , available for refilling by liquids that wet but do not swell the poly(Styco-DVB) particulates enmeshed in PTFE. Examples of such liquids are *n*-hexane, *n*-heptane, *n*-hexadecane, methanol, ethanol, *n*-propanol, *n*-butanol, and n-hexanol. To demonstrate that the volume of such organic liquids,  $V_0^0$  (mL/g of dry composite) reabsorbed by the composite is indeed equal within experimental error to the original volume of water of composition  $V_0^w$  (mL/g of dry composite) the average  $V_0^0$  observed for the above eight organic liquids was compared with the average  $V_0^w$  for five determinations of the original water content. These data, collected in Table I, verify the expected agreement for each of the six composite poly(Sty-co-DVB) samples; that is, the difference  $(V_0^0)_i - V_0^w$  was  $\pm 0.2$ . Since  $V_0^0$  was determined in the manner to be utilized in the analytic procedure,  $V_0^0$  was selected in preference to  $V_0^w$  as the appropriate factor to use for calculating the available void space  $V_0$  in each composite sample; that is,  $V_0 = W_0 V_0^0$ , where  $W_0$  is the dry weight of the composite sample used to absorb the total volume  $V_s$  of liquid. The difference  $V_s - V_0$  is the volume of liquid absorbed by the poly(Sty-co-DVB) contained in the sample.

The data collected in Table I also show that  $V_{\bar{0}}^{0}$  is independent of the DVB mole fraction r of the copolymer, which verifies that the eight liquids named above do not cause measurable swelling even when r is only 0.01; these liquids merely refill the void space by capillary action. Our kinetic studies showed that this occurs within minutes after making surface contact, as noted in Fig. 8 of Ref. 2.

In applying the correction for void volume  $V_0$ , it is realized that the volume not occupied by gelled particulate and PTFE microfibers will change with swelling. The change, however, is a fraction of a small number, and since it should be a linear function of swelling, it is believed that this inconstancy will not significantly affect the observed relative swelling power of the test liquids determined for a given set of copolymers. The measurement of  $V_0$  and x are considered to be the largest sources of error in the determination of S. Because S is proportional to  $\Delta V = V_s - V_0$ , it is obvious that the values for S for liquids with good swelling power are more reliable than those for liquids with poor swelling power.

## Study of Swelling as a Function of Cross-link Density

For the purpose of this study, the cross-link density,  $\rho$  is defined as the ratio of the number of atoms that form cross-linking junctions to the total number of atoms in the backbones of the segments that constitute the cross-

linked network. For poly(Sty-co-DVB),  $\rho$  is given by

$$\varphi = \frac{r}{(1+r)}$$

where r is the mole fraction of DVB in the polymer. The average number of atoms  $\lambda$  in the backbone of the polystyrene segments between cross-link junctions is the inverse of the cross-link density; that is,  $\lambda = 1/\rho$ .

In Staudinger's classic studies of Sty-co-DVB polymer swelling,<sup>3</sup> the swelling ratio  $(V_g - V_p)/V_p$  was plotted as a function of  $R_c$ , the monomer charge ratio of DVB to Sty made to undergo polymerization, which showed that swelling decreases inversely to  $R_c$ . He also noted that the volume ratio is not linear with  $1/R_c$ . The product of swellability S as reported in this study times the density d of the liquid absorbed by the polymer is the equivalent of the volume ratio reported by Staudinger, and our  $\varphi$  is a function of his  $R_c$ . Not surprisingly, therefore, we also noted that S decreases with  $\varphi$  (Fig. 2a) and that S is not a linear function of  $\lambda = 1/\varphi$  (Fig. 2b). On further consideration of these data, however, we noted that S is indeed a linear function of  $\varphi^{-1/3}$ , and for swelling in benzene (Fig. 2d) it is given by

$$S = 2.14 \left( P^{-1/3} - 1.70 \right) = 2.14 \left( \lambda^{1/3} - 1.70 \right)$$

Such linear relationships are very reproducible, as indicated by the data summarized in Fig. 3, which shows the results for five replicate studies of poly(Sty-co-DVB) swelling in toluene. The average **S** of the five observed *S* at a given  $\rho^{-1/3}$  is shown as an open circle, and the range of these data is indicated by a vertical bar through the open circle. The best line through each set of six data points of a given replicate were straight lines that were virtually superimpossible upon the line shown in Fig. 3. These lines are given by

$$S = 2.02 \pm 0.01 [\varrho^{-1/3} - (1.75 \pm 0.05)]$$

This degree of reproducibility convinced us that it is only necessary to make one study of swelling as a function of  $\varrho = 1/\lambda$  in order to obtain a reliable measure of the slope of the line obtained thereby, that is, the relative swelling power *C* of the test liquid.

Accordingly, similar swelling studies using the same set of six composite film samples were made using a variety of liquids (Table II). The plot of the data for each study was a straight line given by

$$S = C(\varrho^{-1/3} - \varrho_0^{-1/3}) = C(\lambda^{1/3} - \lambda_0^{-1/3})$$

where  $\rho_0 = 1/\lambda_0$  is the critical cross-link density of Sty-co-DVB polymers at or above which S = 0, that is, within experimental error of the procedure.

The constants C and corresponding  $\rho^{-1/3}$  observed for the set of liquids studied in this investigation are collected in Table II. The observed C range from 2.25 for dimethylaniline to zero for *n*-butanol, whereas the corresponding observed  $\rho_0^{-1/3}$  appear to be statistically constant at 1.77  $\pm$  0.13.



Fig. 3. Volume S (mL) of toluene absorbed per gram of poly(Sty-co-DVB) at equilibrium swelling as a function of  $\rho^{-1/3}$ . The center of the open circles represents the corresponding average of five replicate determinations for the copolymer with cross-link density  $\rho$ . The length of the vertical bar through each open circle represents the range of the data for that set of five measurements.

# **Theoretical Consideration of Swelling**

That swelling S should be related linearly to  $P^{-1/3} = \lambda^{\nu_3}$  can be shown by consideration of the opposing forces extant at the equilibrium state of polymer swelling in excess liquid. It was pointed out by Flory<sup>5</sup> that a close analogy exists between swelling equilibrium and osmotic equilibrium. In the former, the gelled network structure performs the multiple role of solute, osmotic membrane, and pressure-generating device. Each segment of length *l* between cross-linked junctions is completely associated with solvent molecules so that the segments are forced to form elongated configurations in a random mode to fill their volume space. A force akin to elastic retraction in rubber develops in opposition to the swelling process. This force increases with swelling as the dilution force decreases, owing to a balance of chemical potential of the solvent inside and outside the gelled polymer. Ultimately, the restraining force of the gelled network becomes



Fig. 4. Volume of liquid S (mL/g) as a function of  $\rho^{-1/3}$  for seven representative liquids, the relative swelling powers of which are in the order N,N-dimethylaniline > anisole > pyridine > n-heptyl acetate, cis-decahydronaphthalene > (trifluoromethyl)benzene > trans-decahydronaphthalene.

equal to the osmotic pressure  $\pi$ , and a state of equilibrium at  $V_g$  is established.

Beginning with this model for equilibrium swelling and assuming that this state is described by van't Hoff's relationship

$$\pi V_{g} = nRT$$

where n is the number of moles of polymer segments, T is temperature, and R is the universal constant in appropriate units, we can move toward the observed empirical relationship, if we accept that  $V_g$  is a linear function of l, which is proportional to  $\lambda$ , the number of carbon atoms in the backbone of the polystyrene segments of length l. Since  $\pi$  is inversely proportional to the radius (if  $V_g$  is considered to a sphere) or to an edge (if  $V_g$  is considered to be a cube), it follows that  $\pi$ , the force per unit area in a given direction that restrains the gel volume to  $V_g = f(\lambda)$ , must be inversely proportion to the cube root of  $V_g$ ; that is,  $\pi = f(\lambda^{-1/3})$ . Substitution for  $\pi$  in the van't Hoff relationship gives

$$V_g = \frac{nRT}{f(\lambda^{-1/3})} = a \ \lambda^{1/3} + b = a \varrho^{-1/3} + b$$

Substituting  $V_g$  in the swelling relationship,  $S = [(V_g/V_0) - l] d$ , gives

$$S = \left(rac{a}{V_0}\lambda^{1/3} + rac{b}{V_0} - l
ight)d^{-1}$$

Since a, b,  $V_0$ , and d are constant at constant temperature T, this relationship reduces to

$$S = A\lambda^{1/3} + B = A\varrho^{-1/3} + B$$

which is exactly the form of the relationship for S in terms of  $\lambda = 1/\rho$  derived empirically.

## SUMMARY AND CONCLUSIONS

It was shown that the procedure for measuring the sorptivity S' (mL liquid absorbed per g composite) of thin microporous composite films consisting of particulate styrene-co-divinylbenzene polymers (80%) enmeshed in PTFE microfibers (20%) can be used to measure the swellability S (mL liquid absorbed per g copolymer) of the particulate contained therein, if appropriate corrections are made to account for the void volume  $V_0$  and the weight fraction of PTFE in the microporous composite film. The latter is determined by elementary analysis for fluorine and the former by measurement of the sorptivity S' for liquids that wet but do not swell the particulate.

This procedure was used to measure S for a set of six Sty-co-DVB polymers, the DVB mole fraction r of which ranged from 0.01 to 0.12. When the observed S in a given liquid was plotted as a function of the cross-link density,  $\rho^{-1/3} = [r/(1 + r)]^{-1/3}$ , straight lines were obtained, which can be represented by the general equation

$$S = C(\varphi^{1/3} - \varphi_0^{-1/3}) = C(\lambda^{1/3} - \lambda_0^{-1/3})$$

where C is a constant characteristic of the relative swelling power of the liquid with respect to Sty-co-DVB polymers and  $\rho_0^{-1/3}$  appears to be statistically constant at 1.77  $\pm$  0.13; that is,  $\rho_0 = 0.18 \pm 0.04$  is the critical cross-link density at or above which S = 0 for the type of Sty-co-DVB polymers used in this investigation.

Having demonstrated this linear relationship, it is now possible to correlate the common charge ratio  $R_c$  reported by earlier investigators<sup>3,4</sup> with the corresponding  $\varphi$ , calculated on the basis of observed S reported by the earlier investigators for a given liquid, and the constants C and  $\varphi_0^{-1/3}$ ,

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determined as described here in the Experimental section.<sup>10,11</sup> It should also be possible to correlate the relative swelling power C for Sty-co-DVB polymers with the molecular structure of the liquid, and since swelling power is related to solvent power, it should also be possible to correlate C with the solubility parameter of the liquid and establish thereby the solubility parameter of the polymer. Conversely, it should be possible to study systematically the effect on C for a given liquid caused by molecular modification of the backbone and pendant groups of the copolymer. The results of such studies will be reported in subsequent publications.

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