between NMR line width and monomer charge ratio reported by the other manufacturers (Table I), emphasizing that the charge ratio of the comonomers made to undergo polymerization cannot be used as a reliable measure of the composition of the polymeric product.

Registry No. (Styrene)·(divinylbenzene) (copolymer), 9003-70-7.

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Polymer Swelling. 4. A Reexamination of Reported Polymer Swelling Studies for Conformance to Equations That Relate Swellability to Cross-Link Density

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ABSTRACT: The styrene–divinylbenzene copolymer swelling studies reported years ago by Staudinger, Boyer, and Rempp have been reexamined to test the validity of the observation made recently that swelling, S, of such polymers is given in terms of cross-link density, $\tilde{\chi}$, by the general equation $S = C(\tilde{\chi}^{-1/3} - \tilde{\chi}_0^{-1/3}) = C(\lambda^{1/3} - \lambda_0^{1/3})$, where $\lambda = 1/\tilde{\chi}$ is the average number of carbon atoms in the "backbone" of the polystyrene segments between cross-link junctions, C is a constant characteristic of the swelling power of the liquid for the kind of polymer being investigated at temperature T, and $\tilde{\chi}_0$ is the critical cross-link density of the polymer at or above which $S = 0$. In every reexamination, S, calculated from the reported swelling data, was a linear function of $\lambda^{1/3}$, calculated from the corresponding reported polymer molecular weight data, but the constants C and $\lambda_0^{1/3}$ depended upon the conditions of copolymerization that affect the λ-distribution. Similar linear relationships appear to obtain for swelling studies of "macronet" cross-linked polyesters reported by Takahashi and perhaps for water-swellable "macronet" cross-linked polyacrylates reported by Refojo. It is concluded that the above linear relationship may be general for cross-linked polymer networks and therefore useful in the planning of future studies aimed at a better understanding of polymer swelling in terms of the molecular structures of the polymer and the swelling liquid.

Introduction

We have reported[1] that thin but tough microporous composite films can be made from particulate cross-linked polymer and poly(tetrafluoroethylene) [PTFE] by a work-intensive procedure using an ordinary rubber mill. Because the particles (>80% by weight) are isolated, evenly distributed in three dimensions, and irreversibly enmeshed in an "open-celled" network of PTFE microfibers (<20%) as shown in Figure 1 of ref 1, these composite films are ideal for studying the absorption of liquids and/or vapors by the major component. Such microporous films made from *non-cross-linked* polymer particulates were used by Fowkes[2] to monitor absorption of organic vapors in his study of acid–base complexes of polymers, and we have used such microporous films made from *cross-linked* polystyrene particles[3] to study polymer swelling in excess liquid as a function of cross-link density $\tilde{\chi} = 1/\lambda$, where λ is the average number of carbon atoms in the "backbone" of the polystyrene segments between cross-link junctions.

It was shown[3] in the latter study that the volume, S, of liquid absorbed by a unit weight of poly(styrene-*co*-divinylbenzene) [poly(Sty-*co*-DVB)] at swelling equilibrium in excess liquid is given by the general equation

$$S = C(\lambda^{1/3} - \lambda_0^{1/3}) = C(\tilde{\chi}^{-1/3} - \tilde{\chi}_0^{-1/3})$$

where C is the swelling power of the liquid at temperature T for the copolymer, and $\tilde{\chi}_0$ is the critical cross-link density of the copolymer, above which $S = 0$ (i.e., not measurable with the experimental procedure of this investigation). It was also shown[4] that the aromatic ^{13}C NMR line width, $\nu_{1/2}$, is related to the cross-link density, determined by means of the above swellability–cross-link density relationship, by the equation

$$\nu_{1/2} = 4.8 \times 10^4 \tilde{\chi}^{-1.62}$$

The purpose of this publication is to report tests of the validity of these equations using swelling data already reported for poly(Sty-*co*-DVB) and "macronet" cross-linked polymers prepared by earlier investigators.

Results and Discussion

(A) Sty-DVB Copolymers Made via Anion Polymerization. Swelling data for Sty–DVB copolymers that have very narrow range molecular weight distributions of the polystyrene segment between "nodules" of divinylbenzene have been reported by Rempp[5–7] and his coworkers. These copolymers were made via anionic polymerization[8] with an efficient bifunctional initiator to produce a very narrow range molecular weight distribution (determined by the monomer-to-initiator ratio) of polymer with "living" carbanions at both ends of its linear chain. Divinylbenzene was then added to produce the corre-

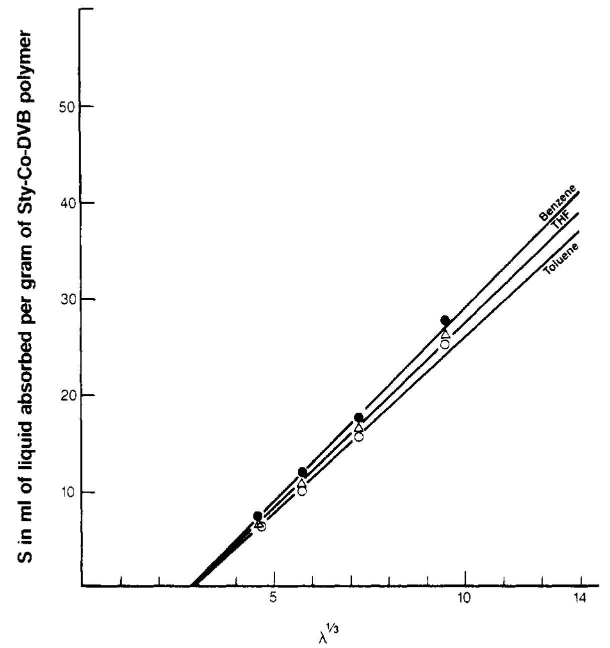


Figure 1. Volume of liquid, S (in mL), absorbed at equilibrium swelling per gram of poly(Sty-*co*-DVB) prepared via anionic polymerization by Rempp[7] in 1970 as a function of the corresponding calculated $\lambda^{1/3}$.

sponding Sty–DVB copolymer[6] with relatively well-defined polystyrene segments of molecular weight M between "nodules" of $(\mathrm{DVB})_n$. The size of these "nodules" and the number of covalently bonded polystyrene segments to a given "nodule" were a function of the molar proportion of DVB added subsequently with respect to the number of moles of available "living" carbanion polystyrene end groups.

$$n\text{-}(\mathrm{CHPhCH_2})_{x/2}(\mathrm{CH_2CHPh})_{x/2}\text{-} + ny\mathrm{DVB} \rightarrow [(\mathrm{Sty})_x(\mathrm{DVB})_y]_n$$

Rempp reported his swelling data as the ratio V_g/V_0, where V_g and V_0 refer respectively to the unit volume of the polymer in the gelled and the dry states as a function of M, the molecular weight of the polystyrene segment between DVB "nodules". These data (Figure 2 and Table 1 of ref 5 and Table 2 of ref 7) were recalculated to give S, in milliliters per gram of polymer, in terms of $(V_g - V_0)/V_0d$, where d is the density of the liquid and M is in terms of $\lambda^{1/3} = (M/52)^{1/3}$, where λ is the number of carbon atoms in the backbone of the polystyrene segment between "nodules". When the calculated values for S were plotted as a function of the calculated $\lambda^{1/3}$, straight lines were obtained as expected. The lines (Figure 1) that represent the set of data published in 1970 (Table 2 of ref 8) are given by the equation

$$S = C(\lambda^{1/3} - 2.75)$$

but the lines (Figure 2) that represent the set of data published in 1978 (Figure 2 and Table 1 of ref 5) are given by

$$S = C(\lambda^{1/3} - 5.0)$$

Why the $\lambda_0^{1/3}$ for Rempp's data[5] published in 1978 (Figure 2; $\lambda_0^{1/3} = 5.0$, i.e., $\tilde{\chi} = 0.008$) is almost twice that for the corresponding constant observed for his data published in 1970 (Figure 1; $\lambda_0^{1/3} = 2.75$, i.e., $\tilde{\chi}_0 = 0.05$) is not understood. The former, however, is unusually high relative to that observed for Sty–DVB Copolymers made via free radical polymerization (Figure 4 of ref 3; $\tilde{\chi}_0^{-1/3} = 1.77$, i.e., $\tilde{\chi} = 0.18$), the linear relationship for which is given by

$$S = C[\lambda^{1/3} - (1.77 \pm 0.13)]$$

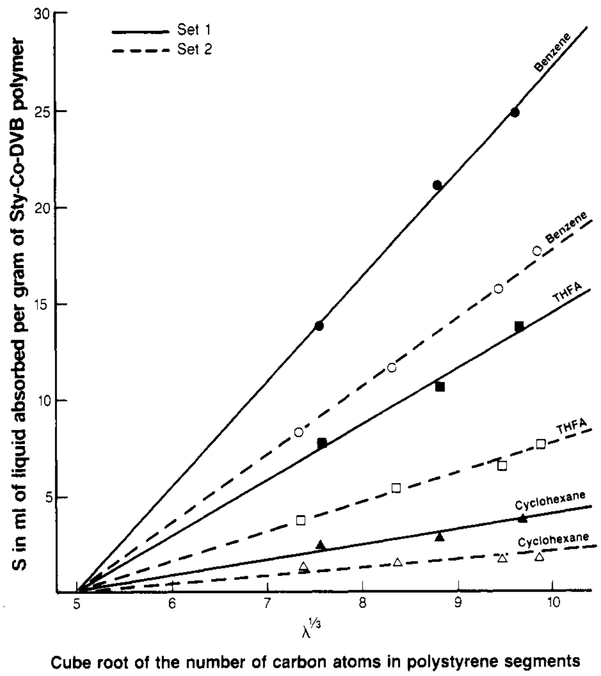


Figure 2. Volume of liquid, S (in mL), absorbed at equilibrium swelling per gram of poly(Sty-*co*-DVB) prepared via anion polymerization by Rempp[5] in 1978, as a function of the corresponding calculated $\lambda^{1/3}$.

Since the latter mode of polymerization is known to give very broad λ-distributions [i.e., $\lambda \pm (a \gg 0)$] relative to the former [i.e., $\lambda \pm (a = 0)$], it is assumed that this observed difference is attributable to the difference in the ranges of the λ-distributions [i.e., $2a$]. It follows, therefore, that copolymers with very narrow λ-distributions should be very sensitive to small changes in a, whereas copolymers with very broad λ-distributions should be relatively insensitive to small change in a.

The marked difference in the linear functions exhibited by polymers made via anionic polymerization and those made via free radical polymerization underlines the importance of using a set of Sty–DVB copolymers made via the same experimental conditions, except for the monomer ratio (Sty/DVB) made to undergo polymerization. This is especially important in the comparison of relative swelling power determined in one laboratory with that determined in another. If the two sets of experimental conditions are not exactly the same, the observed swelling power for a given liquid cannot be exactly the same. One should be proportional to the other, however, and consequently the relative swelling power for a series of liquids should be in the same order.

The relative swelling powers of benzene ($C_{1\mathrm{B}} = 5.4$), tetrahydrofurfuryl alcohol ($C_{1\mathrm{THFA}} = 2.9$) and cyclohexane ($C_{1\mathrm{C}} = 0.8$) observed for the first set of copolymers reported by Rempp in 1978 (solid line, Figure 2) are uniformly about 1.8-fold greater than the corresponding relative swelling powers ($C_{2\mathrm{B}} = 3.5$, $C_{2\mathrm{THFA}} = 1.6$, $C_{2\mathrm{C}} = 0.4$) calculated for the second set of copolymers reported in 1978 (dashed line, Figure 2). It is suspected that this difference may be attributable to the relative amount of DVB added to the available polystyrene carbanion end groups to convert the "living" polystyrene polymers to the corresponding cross-linked polymer network. This rationale is consistent with the expectation that the swelling power of a given

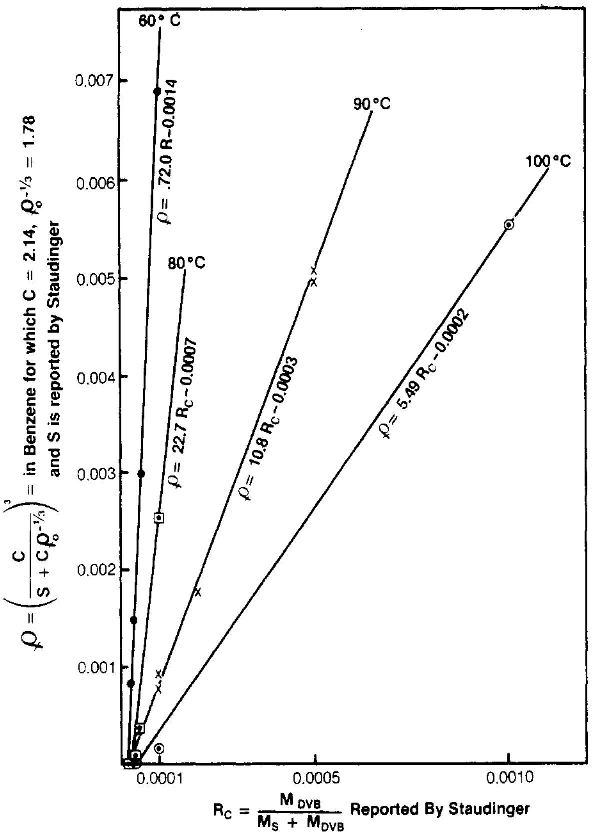


Figure 3. Calculated cross-link density, $\tilde{\chi}$, of poly(Sty-*co*-DVB) prepared via free-radical polymerization by Staudinger[9] as a function of the mole fraction, R_c, of DVB monomer made to undergo copolymerization with styrene monomer at temperature T.

liquid with respect to a cross-linked polymer will be a function of the molecular structure of the cross-linking "nodules" and that of the pendant groups, as well as of the number of carbon atoms in the backbone of the polymer segment between cross-link junctions.

(B) Styrene–Divinylbenzene Copolymers Made via Free Radical Polymerization. The earliest swelling studies of Sty–DVB copolymers made via free radical polymerization (which is known to afford cross-linked polymer with a wide range λ-distribution) were reported by Staudinger[9] and later by Boyer.[10] In these now classical studies, the increase in volume caused by swelling was reported as $(V_g/V_0 - 1)$ by Staudinger and as V_g/V_0 by Boyer, and these ratios were correlated with the molar monomer ratio DVB/Sty [equal approximately to DVB/(Sty + DVB) = R_c] made to undergo polymerization at temperature T. Consequently, it was not possible to know with certainty the corresponding mole fraction of DVB actually incorporated in the residual insoluble polymer after exhaustive extraction of soluble homopolymer from the polymer mixture. Nevertheless, it was possible to use the reported swelling data (after conversion to S) that were measured in benzene, carbon tetrachloride, and cyclohexane to calculate the corresponding cross-link density of their residual insoluble polymers by means of a rearranged form of the swellability equation

$$\tilde{\chi} = [C/(S + C\tilde{\chi}_0^{-1/3})]^3$$

where C and $\tilde{\chi}_0$ are the constants for the above liquids established in our swellability studies.[3]

When the $\tilde{\chi}$ calculated for Staudinger's copolymers was plotted as a function of the DVB mole fraction, R_c, made to copolymerize with styrene at temperature T, straight lines were obtained (Figure 3) given by $\tilde{\chi} = rR_c - B$; when log $(\Delta\tilde{\chi}/\Delta R_c)$ = log r (i.e., the log of the slope of these lines) was plotted in turn as a function of $1/T$, an Arrhenius-like relationship was obtained (Figure 4), i.e.

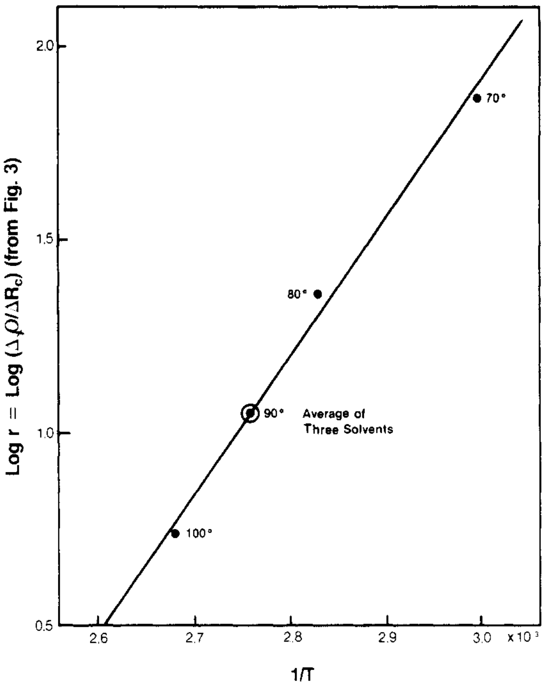


Figure 4. log $(\Delta\tilde{\chi}/\Delta R_c)$, i.e., the slope of the lines in Figure 3, as a function of $1/T$.

$$\log r = [(E_2 - E_1)/2.3R](1/T) + K$$

where E_1 and E_2 are the activation energies for polymerization of DVB and styrene, respectively. From the slope of this line (Figure 4), ΔE was calculated to be about 8 kcal.

A straight-line relationship as also obtained for the swelling data reported by Boyer,[10] who caused free radical polymerization to occur at 105 °C. This relationship is given by

$$\tilde{\chi} = 9.21R_c - 0.0024$$

whereas the corresponding relationship deduced for the swelling data reported by Staudinger (Figure 3) for his copolymers made at 100 °C is given by

$$\tilde{\chi} = 5.49R_c - 0.0002$$

Again, the difference in these two linear relations is believed to be attributable to small differences in the conditions for free radical polymerization used in the respective laboratories. Unfortunately these conditions were not described in enough detail to determine whether this is indeed the case.

The linear relationships (noted in Figures 3 and 4) for $\tilde{\chi}$ show that the relative solvent power determined in our laboratory for a given liquid is proportional to, if not the same as, the swelling power noted in other laboratories using another set of Sty–DVB copolymers made via free radical polymerization. This supports the point of view that if the conditions for making the set of Sty–DVB copolymers via free radical polymerization are identical except for the molar ratio of Sty/DVB, the swelling power, C, observed in the two laboratories should be identical.

(C) "Macronet" Cross-Linked Polyesters and Polyacrylates. Swelling data for "macronet" cross-linked polyesters were reported by Takahashi.[11] His cross-linked polymers were prepared stepwise as follows: To a mixture of maleic anhydride and succinic acid was added propylene glycol in equivalent amount to the molar sum of the other two components. The mixture was made to undergo pol-

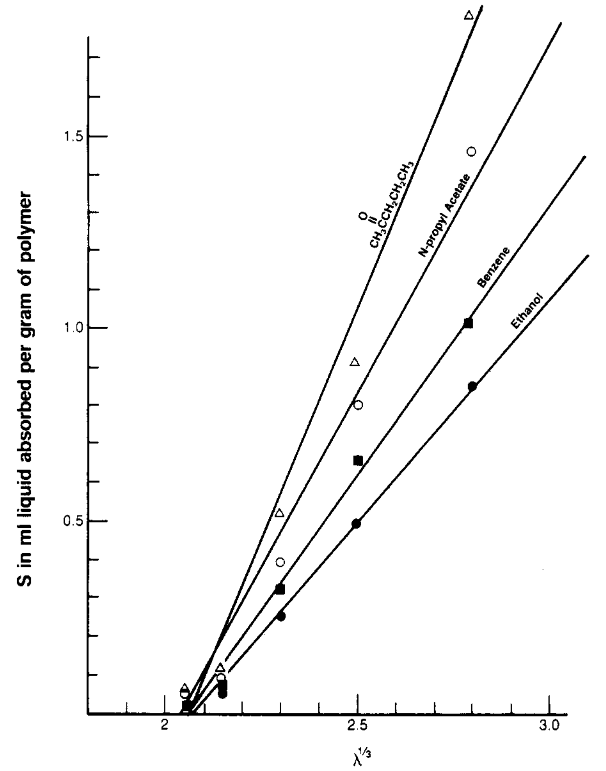
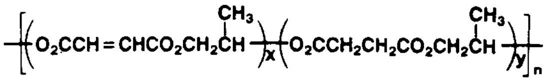


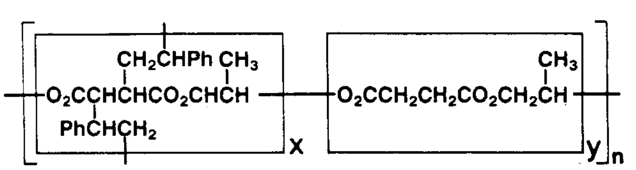
Figure 5. Volume of liquid, S (in mL), absorbed at equilibrium swelling per gram of cross-linked polyester prepared by Takahashi[11] in 1983 as a function of calculated $\lambda^{1/3}$.

ycondensation at 220 °C to give the corresponding polyester.



$$-\!\left[\left(O_2CCH{=}CHCO_2CH_2\overset{CH_3}{C}H\right)_x\left(O_2CCH_2CH_2CO_2CH_2\overset{CH_3}{C}H\right)_y\right]_n\!-$$

This unsaturated polyester was dissolved in styrene, the molar amount of which was twice that of the unsaturated groups contributed by the maleic component. The resultant solution was poured between two glass plates spaced 1 mm apart and then made to polymerize in place by the addition of trace peroxide to obtain the corresponding saturated terpolymer cross-linked with styrene, which was then used for his swelling studies in various solvents.



$$\left[\left(\begin{array}{c} CH_2CHPh\;CH_3 \\ O_2CCHCHCO_2CHCH \\ PhCHCH_2 \end{array}\right)_x\left(\begin{array}{r} CH_3 \\ O_2CCH_2CH_2CO_2CH_2CH \end{array}\right)_y\right]_n$$

The average number of atoms, λ, in the "backbone" of the segment between cross-linked junctions in such a "macronet" structure is given by the ratio of the total number of atoms in the backbones of the cross-linked network divided by the total number of atoms that form cross-link junctions. In this "macronet" polymer system λ is given by

$$\lambda = (6x + 4y)/x$$

where x and y are as defined in the cross-linked polymer structure shown above. The λ calculated from Takahashi's data for his samples 1–5 (Table 1 of ref 11) were 22, 15.3, 12, 10, and 8.7. The corresponding $S = [V_g/V_0 - 1]/d$ was calculated by using the swelling ratios V_g/V_0 reported by Takahashi for the solvents listed in Table 3 of ref 11. In each case, the calculated swellability, S, increased linearly with the corresponding calculated $\lambda^{1/3}$ (Figure 5), as given by the general equation

$$S = C[\lambda^{1/3} - (2.05 \pm 0.05)]$$

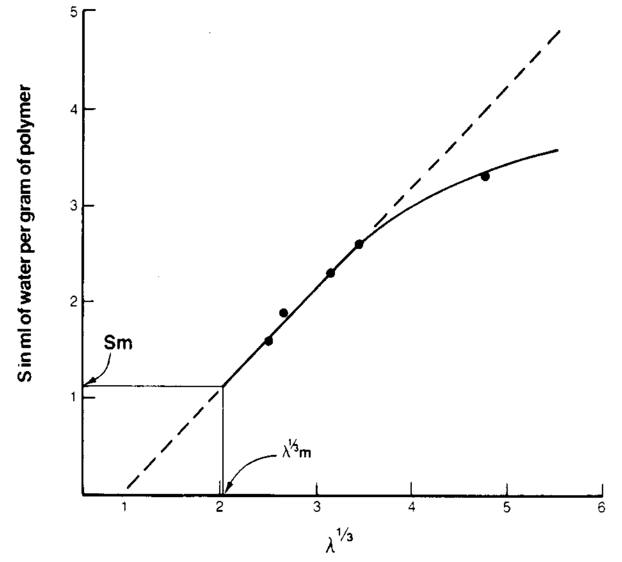
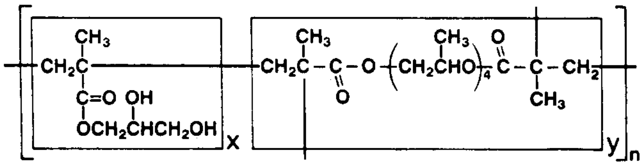


Figure 6. Volume of water, S (in mL), absorbed at equilibrium swelling per gram of GlyMA–TEGDMA copolymers prepared by Refojo[12] in 1965 as a function of calculated $\lambda^{1/3}$.

The $\lambda_0^{1/3}$ observed for these studies (i.e., $\bar{\chi} = 0.12$) is in the range of the $\lambda_0^{1/3}$ observed by us[3] for poly(Sty-*co*-DVB), i.e., $\lambda_0^{1/3} = 1.77 \pm 0.13$, $\bar{\chi}_0 = 0.18$.

An approximately linear relationship of S in terms of $\lambda^{1/3}$ also obtains for hydrophilic "macronet" cross-linked polymers as indicated by the results deduced via a similar reconsideration of the swelling and molecular weight data reported by Refojo,[12] who studied aqueous swelling of 2,3-dihydroxypropyl methacrylate–tetraethylene glycol dimethacrylate copolymers.



$$\left[\left(\begin{array}{l} CH_3 \\ CH_2C \\ C{=}O\;\;OH \\ OCH_2CHCH_2OH \end{array}\right)_x\left(\begin{array}{l} CH_3 \qquad\qquad\qquad CH_3\;\;O \\ CH_2C-C-O(CH_2CHO)_4C-C-CH_2 \\ \qquad\;\; O \qquad\qquad\qquad\quad CH_3 \end{array}\right)_y\right]_n$$

In these cross-linked "macronet" copolymers, λ is given by

$$\lambda = (2x + 19y)/2y$$

Thus, the λ calculated from the reported percent TEGDMA content for the five copolymers prepared by Refojo (Figure 2 of ref 12) are 109, 41, 32, 19, and 17, and the corresponding $S = (V_g/V_0 - 1)/d$ calculated from the V_g/V_0 data reported by Refojo in Figure 2 of ref 12 are 3.3, 2.6, 2.3, 1.9, and 1.6 mL of water absorbed per gram of cross-linked polymer. The plot of these calculated data for S in terms of the calculated data for $\lambda^{1/3}$ (Figure 6) shows that all but one of the data points fits well on the line given by

$$S = 1.08(\lambda^{1/3} - 1)$$

It is suspected, however, that deviation from linearity at high mole fraction of the comonomer may be the rule for "macronet" cross-linked polymers of the type X–Y, because the observed S is a function of two variables that change with the mole fraction of monomer Y that provides the cross-linking junctions, i.e., $\bar{\chi}$ and the relative affinity of the solvent for the components X and Y. Thus, the relatively low S at $\lambda^{1/3} = 4.78$ in Figure 6 may reflect a lower affinity of water for the 2,3-dihydroxypropyl methacrylate (component X) relative to the corresponding affinity for tetraethylene glycol dimethacrylate (component Y), the cumulative effect of which can be significantly large at high X/Y relative to that at low X/Y. In experiments designed to study S as a function of $\lambda = 1/\tilde{\chi}$, it is important, therefore, to choose comonomers X and Y such that the solvent affinity difference will be minimal if not zero.

Another characteristic of "macronet" cross-linked polymers that should be noted is that the lowest possible λ is λ_m. For a given "macronet" poly(X-*co*-Y), λ_m is attained when Y, the component that provides the cross-linking junctions, is made to undergo "homopolymerization". For the study summarized in Figure 6, λ_m is 8.5, which means that the least attainable swelling for the copolymer in question is $S_m = 1.12$, which occurs at $\lambda_m^{1/3} = 2.04$. All S for $\lambda^{1/3} < 2.04$ are unattainable with the given pair of comonomers; $S = 0$ at $\lambda_0 = 1$ can be attained with a pair of such comonomers only if it were possible for every atom in the backbone to be a cross-link junction.

Summary and Conclusions

The linear relationship of polymer swelling, S, in terms of cross-link density, $\tilde{\chi}$, as given by

$$S = C(\tilde{\chi}^{-1/3} - \tilde{\chi}_0^{-1/3}) = C(\lambda^{1/3} - \lambda_0^{1/3})$$

appears to obtain for most types of cross-linked polymer systems, including some "macronet" cross-linked polymers.

Cross-link density, $\tilde{\chi}$, is defined here as the inverse of λ, the average number of atoms in the backbone of the polymer segments between cross-link junctions. For poly(Sty-*co*-DVB) and for macronet cross-linked polymers of the type poly(X-*co*-Y), where Y is the cross-linking monomer, λ is given by

$$\lambda = (x\mathrm{X} + y\mathrm{Y})/z\mathrm{Y}$$

where x and y are the number of atoms in monomers X and Y, respectively, that contribute to the "backbones" of the polymer segments between and including the cross-link junctions and z is the number of atoms in Y that form cross-link junctions.

The constant $\tilde{\chi}_0 = 1/\lambda_0$ represents the critical cross-link density for X–Y copolymers, above which $S = 0$ (i.e., not measurable with the experimental procedure of this investigation). The constant $\tilde{\chi}_0$, therefore, is a measure of the polymer's sensitivity to swelling, which for the same X/Y ratio of a given X–Y copolymer is related inversely to the breadth of the λ-distribution of that polymer. The swelling sensitivity for copolymers with broad λ-distributions $\tilde{\lambda} \pm (a \gg 0)$ (i.e., $\tilde{\chi}_0 = 0.18$) is considerably greater than that observed for copolymers with well-defined narrow λ-distributions $\lambda \pm 0$ (i.e., $\tilde{\chi}_0 = 0.008$–0.05), which suggests that it may be possible to characterize the range of a λ-distribution in terms $\Delta\tilde{\chi}_0$, when $\tilde{\chi}_0$ for polymers with well-defined λ-distributions can be characterized with certainty.

If the apparent sensitivity in observed $\tilde{\chi}_0$ for small differences in variance in the λ-distributions of polymers with very narrow λ-distributions is real, then it may be better from the standpoint of reproducibility to compare swelling of polymers with very broad λ-distributions, which appear to be relatively insensitive to small changes in variance.

The constant C is a measure of the relative swelling power of a given liquid for a set of X–Y copolymers that were prepared under the same experimental conditions for polymerization except for the X/Y monomer ratio. Thus, one should be able to use the same set of X–Y copolymers to study C as a function of the molecular structure of the swelling liquid or conversely to use a given liquid or a set of liquids to study C as a function of the molecular structure of the X–Y copolymer.

Since swelling power is related to solvent power, it should be possible to correlate C with Hildebrand's solubility parameter and thus help clarify concepts and ideas developing in this area of science.[13] Since solubility and swelling are both important considerations in separations using ultrafiltration and reverse osmosis membranes,[14] these relationships should be useful in this area of science as well; lastly, since chromatography involves surface adsorption and desorption, which is related to surface solubility, it may be possible to utilize the above principles to gain a better understanding of chromatographic separations that involve polymeric substrates.

The results of studies of the types alluded to above will be reported in subsequent publications.

Registry No. Poly(Sty-*co*-DVB) (copolymer), 9003-70-7; (maleic anhydride)·(succinic acid)·(propylene glycol) (copolymer), 87278-97-5; styrene, 100-42-5; (2,3-dihydroxypropyl methacrylate)·(tetraethylene glycol dimethacrylate) (copolymer), 99797-26-9.

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