(5) McCormick, C. L.; Blackmon, K. P.; Elliott, D. L., to be published in *J. Polym. Sci., Polym. Chem. Ed.*
(6) McCormick, C. L.; Elliott, D. L. *Macromolecules* **1986**, *19*, 542.
(7) Harwood, H. J.; Ritchey, S. *Polym. Lett.* **1964**, *2*, 601.
(8) Igarashi, S. *J. Polym. Sci., Polym. Lett. Ed.* **1963**, *1*, 359.
(9) Carreau, P. J.; Dekee, D.; Daroux, M. *Can. J. Chem. Eng.* **1979**, *57*, 135.
(10) Billmeyer, F. W. *Textbook of Polymer Science*, 2nd ed.; Wiley Interscience: New York, 1971; p 86.
(11) Arai, F. Master's Thesis, University of Southern Mississippi, Hattiesburg, MS, 1984.
(12) Neidlinger, H. H.; Arai, F. *DOE Contract No. DE-AS19-80BC10321, Fifth Annual Report*, 1982.
(13) Tan, J. S.; Gasper, S. P. *Macromolecules* **1973**, *6*, 741.
(14) Katchalsky, A.; Spitnik, P. *J. Polym. Sci.* **1947**, *2*, 432.
(15) Kulicke, W. M.; Kniewske, R. *Makromol. Chem.* **1980**, *181*, 823.
(16) Kulicke, W. M.; Kniewske, R. *Makromol. Chem.* **1981**, *182*, 2277.
(17) Manning, G. S. *Acc. Chem. Res.* **1979**, *12*, 443.
(18) McCormick, C. L.; Blackmon, K. P. *Macromolecules*, preceding paper in this issue.

Polymer Swelling. 5. Correlation of Relative Swelling of Poly(styrene-*co*-divinylbenzene) with the Hildebrand Solubility Parameter of the Swelling Liquid

L. A. Errede

3M Science Research Laboratories of Central Research, 3M Center, Building 201-2N-22, St. Paul, Minnesota 55144. *Received October 17, 1985*

ABSTRACT: The swellability, S, of styrene-*co*-divinylbenzene polymers in 20 aromatic and 24 aliphatic liquids was studied as a function of cross-link density, λ^{-1}, from $\lambda^{-1} = 0.01$ to $\lambda^{-1} = 0.12$. In every study the relationship was given by $S = C(\lambda^{1/3} - \lambda_0^{1/3})$, where λ 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 λ_0^{-1} is the critical cross-link density, above which $S = 0$. The observed C was correlated with the corresponding known Hildebrand solubility parameter, δ, for five liquid classifications. The solubility parameter of the polymer, δ_{Sty}, determined thereby was 9.5 for substituted benzenes, 9.2 for chlorocarbons, 9.1 for ketones, 8.4 for esters, and 7.3 for ethers. this set of observed δ_{Sty} spans the range reported by earlier investigators, i.e., $\delta_{\mathrm{Sty}} = 8.6$–$9.7$. The plots of C as functions of the corresponding $(\delta_{\mathrm{Sty}} - \delta_{\mathrm{liq}})^2$ for the homologous series of liquids $Z(CH_2)_nH$, where $n < 5$, are almost parallel lines given approximately by $C = A - 0.60(\delta_{\mathrm{Sty}} - \delta_{\mathrm{liq}})^2$, where A is 2.19 for $Z = Ph$, 1.48 for $Z = RCO_2$, 1.42 for $Z = RCO$, and 0.64 for $Z = RO$. Apparently, the major factor that determines swelling power is the relative affinity of Z for the polymer. The cumulative contribution to swelling power owing to the $(CH_2)_nH$ group is only a mitigating factor superimposed on the former.

Introduction

We reported[1] that the magnitude of swelling of a polymer, S (in milliliters of liquid absorbed per gram of polymer in equilibrium with excess liquid), can be measured conveniently and reproducibly after the polymer is comminuted and then fabricated into a thin (<0.3 mm), but tough (tensile strength >250 psi), microporous (>0.5 porosity) composite membrane consisting of the particulate polymer (>80% by weight) enmeshed in poly(tetrafluoroethylene) microfibers (<20%). We correlated S with the corresponding cross-link density, λ^{-1}, of styrene-*co*-divinylbenzene polymers, which ranged from $\lambda^{-1} = 0.01$ to $\lambda^{-1} = 0.12$, and we showed[2,3] that S is related to λ^{-1} by

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

where λ is the average number of carbon atoms in the backbone of the polystyrene segments between cross-link junctions, λ_0^{-1} is the critical cross-link density of the polymer, above which $S = 0$, and C is the relative swelling power of the liquid.

It is well-known that swelling power is related to solvent power,[4] which can be expressed in terms of the Hildebrand solubility parameter,[5] δ, and that the solubility of a given solute with solubility parameters δ_{sol} in a given liquid with solubility parameter δ_{liq} is maximal when $(\delta_{\mathrm{sol}} - \delta_{\mathrm{liq}})^2$ is zero. Gee[6] has shown that a similar relationship appears to obtain for swelling of cross-linked polymers; i.e., swelling is maximal when $(\delta_{\mathrm{p}} - \delta_{\mathrm{liq}})^2$ is zero, where δ_{p} is the solubility parameter of the polymer. It was of interest, therefore, to attempt measurement of δ_{Sty} for poly(Sty-*co*-DVB) on the basis of the swelling power, C, observed by us as a function of the corresponding δ_{liq} reported by others[7-10] and then to compare the observed $\delta_{\mathrm{Sty}} = \delta_{\mathrm{liq}}$ at C_{max} with the corresponding δ_{Sty} determined experimentally by others[7,8,11-13] on the basis of maximal solubility. The latter varied from $\delta_{\mathrm{Sty}} = 8.6$ to 9.7 in $\mathrm{cal}^{1/2}/\mathrm{cm}^{3/2}$.

The purpose of this publication is to report the results of our correlation that was aimed at a possible explanation for the wide range of δ_{Sty} observed experimentally by earlier investigators.

Experimental Section

The procedure for making thin microporous composite films from poly(Sty-*co*-DVB) particular and PTFE emulsion is described[1] in detail in part 1. The procedure for measuring S, in milliliters of absorbed liquid per gram of polymer, is described[2] in detail in part 2. The set of six composite films that were used previously to study S as a function of $\lambda^{1/3}$ in 19 organic liquids (Table 1 of ref 2) were again used to establish the characteristic linear relationship (Figures 3 and 4 of ref 2) for the 20 aromatic and 24 aliphatic liquids listed in Tables I and II. The liquids tested were obtained from commercial sources, usually Aldrich Chemical Co., and they were used without further purification.

Results and Discussion

The 44 compounds listed in Tables I and II were selected for this correlation of poly(Sty-*co*-DVB) swelling power, C, with the corresponding Hildebrand solubility parameter, δ, on the basis of the following criteria: (1) the melting point of the compound was <20 °C and the boiling point was >40 °C; (2) the corresponding Hildebrand solubility parameter of the liquid was published in the scientific

0024-9297/86/2219-1522$01.50/0 © 1986 American Chemical Society

Table I
Correlation of C with Solubility Parameters Reported for Substituted Benzenes (δ_{Sty} = 9.5, Figure 1)

liquid	C	$\lambda_0^{1/3}$	δ_{liq}	ref	$(\delta_{Sty} - \delta_{liq})^2$
aniline	1.49	1.85	10.42	7	0.85
iodobenzene	1.93	1.80	10.13	7	0.40
o-dichlorobenzene	1.95	1.75	10.04	7	0.27
bromobenzene	2.06	1.80	9.87	7	0.14
m-dichlorobenzene	2.05	1.78	9.80	7	0.09
acetophenone	1.88	1.93	9.68	7	0.03
chlorobenzene	2.18	1.80	9.67	9	0.03
N,*N*-dimethylaniline	2.25	1.80	9.84	7	0.11
tetrahydronaphthalene	2.22	1.90	9.50	9	0.00
benzene	2.14	1.70	9.16	7	0.12
fluorobenzene	1.98	1.75	9.11	7	0.15
o-xylene	2.02	1.70	9.06	7	0.19
toluene	2.02	1.75	8.93	7	0.32
m-xylene	1.80	1.70	8.88	7	0.38
p-xylene	1.73	1.75	8.83	7	0.45
(trifluoromethyl)benzene	0.71	1.85	8.22	7	0.71
ethylbenzene	1.84	1.78	8.84	7	0.44
n-propylbenzene	1.78	1.78	8.65	9	0.74
n-butylbenzene	1.69	1.95	8.58	7	0.85
isopropylbenzene	1.65	1.75	8.60	7	0.81

Table II
Correlation of C with Hildebrand Solubility Parameters Reported for Aliphatic Liquids

liquid	C	$\lambda_0^{1/3}$	δ_{liq}	ref	$(\delta_{Sty} - \delta_{liq})^2$
Ketones: δ_{Sty} = 9.1 at Maximal C as a Function of δ_{liq}					
$CH_3CO(CH_2)_6H$	1.31	1.95	8.50	9	0.36
$H(CH_2)_2CO(CH_2)_7H$	1.04	1.81	8.52	7	0.36
$H(CH_2)_3CO(CH_2)_3H$	1.36	1.90	8.70	7	0.16
$CH_3CO(CH_2)_5H$	1.47	1.95	8.84	9	0.07
$CH_3CO(CH_2)_3H$	1.37	1.75	8.92	9	0.03
$H(CH_2)_2CO(CH_2)_2H$	1.52	1.75	9.06	7	0.002
$CH_3CO(CH_2)_2H$	1.11	1.75	9.45	7	0.12
Esters: δ_{Sty} = 8.4 at Maximal C (Estimated Graphically)					
$CH_3CO_2(CH_2)_4H$	1.46	1.70	8.69	7	0.08
$CH_3CO_2(CH_2)_3H$	1.33	1.60	8.80	7	0.16
$CH_3CO_2(CH_2)_2H$	1.13	1.80	8.91	7	0.26
$CH_3CO_2CH_3$	0.86	1.70	9.43	7	1.06
Ethers: δ_{Sty} = 7.3 at Maximal C (Estimated Graphically)					
Et_2O	0.64	1.60	7.53	7	0.05
n-Bu_2O	0.51	1.50	7.76	7	0.21
n-Hex_2O	0.41	1.50	8.01	7	0.50
Chlorocarbons: δ_{Sty} = 9.2 at Maximal C					
$H(CH_2)_4Cl$	1.42	1.70	8.46	7	0.55
$H(CH_2)_3Cl$	1.63	1.69	8.50	7	0.49
CCl_4	1.97	1.70	8.55	9	0.42
CH_3CHCl_2	1.68	1.70	8.92	7	0.08
$CHCl_3$	2.32	1.70	9.16	7	0.002
$Cl_2CHCHCl_2$	2.29	1.90	9.16	7	0.002
$ClCH_2CHCl_2$	2.04	1.75	9.16	7	0.002
$CCl_2{=}CCl_2$	1.96	1.75	9.28	7	0.006
$ClCH_2CH_2Cl$	1.79	1.78	9.86	7	0.44
CH_2Cl_2	1.99	1.70	9.88	7	0.46

literature; (3) the liquid was available commercially. These liquids were classified into five categories: (1) substituted benzenes, (2) aliphatic ketones, (3) aliphatic esters, (4) aliphatic ethers, and (5) aliphatic chlorocarbons (Tables I and II).

The results obtained in each of these studies of swellability in a given liquid as a function of λ^{-1}, from 0.01 to 0.12, verified the linear relationship stated in eq 1. The relative poly(Sty-*co*-DVB) swelling power, C, for the organic liquids studied thus far ranged from 0 to 2.32, but the corresponding $\lambda_0^{1/3}$ was statistically constant within each liquid classification (i.e., 1.77 ± 0.07 for substituted benzenes, 1.84 ± 0.09 for the aliphatic ketones, 1.76 ± 0.08 for aliphatic chlorocarbons, 1.70 ± 0.08 for aliphatic esters, and 1.53 ± 0.05 for aliphatic ethers).

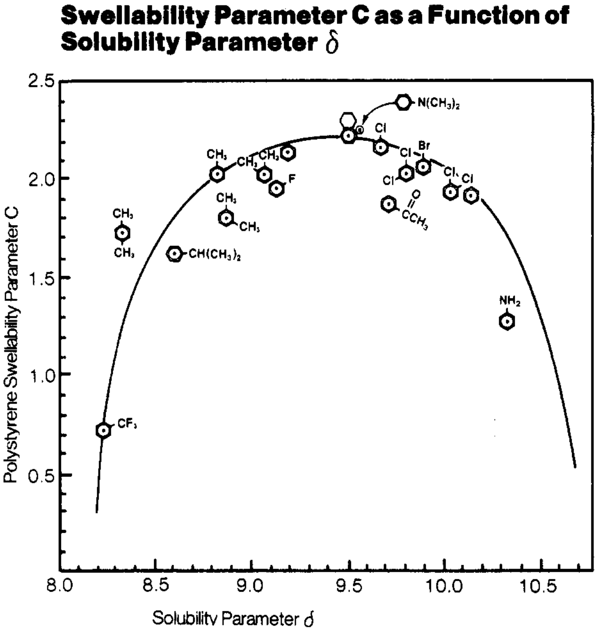

Figure 1. Correlation of observed relative swelling power for poly(Sty-*co*-DVB) with the corresponding reported[7] solubility parameter (δ_{liq}) for the aromatic liquid.

When C for the aromatic liquids listed in Table I was plotted as a function of the corresponding δ_{liq}, a parabolic curve was obtained (Figure 1). Accordingly, the solubility parameter for poly(Sty-*co*-DVB) was taken to be δ_{Sty} = 9.5, where C = 2.25 was maximal at δ_{liq} = 9.5 cal$^{1/2}$/cm$^{3/2}$. The observed δ_{Sty} is in very good agreement with the value (9.4) reported by Hoy.[7] When the corresponding data collected for the aliphatic liquids (Table II) are treated in the same way, however, it is noted immediately that δ_{Sty} obtained thereby reflects the class of liquids chosen to make the correlation. Thus, δ_{Sty} is 9.5 for aromatic compounds, but it is 9.2 for chlorocarbons, 9.1 for ketones (which agrees well with the value reported by Scott and Magat[12,13] and by Boyer[11]), 8.4 for esters, and 7.3 for ethers. This set of observed δ_{Sty} determined on the basis of maximal swelling spans the range of observed δ_{Sty} (i.e., 8.6–9.7) determined by earlier investigators[7,8,11–13] on the basis of maximal solubility. This implies that the molecular geometry of solvation (i.e., the mode of association of the function group, Z, of the solvent molecule with the phenyl group of the polymer and the concomitant association of the remaining part, Y, of the solvent molecule with the backbone of the polymer) may not be the same for each class of liquids of molecular structure Z–Y. The geometry of the polymer may be more suited to accommodate one class of Z–Y better than another, owing to the combination of electronic and steric considerations, and consequently δ_{Sty} = δ_{liq} at maximal solubility (or swelling) for a given solute will vary accordingly, as observed in these studies.

When C for the aromatic liquids (Table I) was plotted as a function of $(9.5 - \delta_{liq})^2$, a straight line was obtained (Figure 2) given by

$$C = 2.22 - 0.95(9.5 - \delta_{liq})^2$$

When the relative swelling powers, C, observed for the liquids in the four sets of homologous series represented by $Ph(CH_2)_nH$ (Table I), $CH_3CO_2(CH_2)_nH$ (Table II), $H(CH_2)_nCO(CH_2)_nH$ (Table II), and $H(CH_2)_nO(CH_2)_nH$ (Table II) were plotted as functions of the corresponding $(\delta_{Sty} - \delta_{liq})^2$, a set of four approximately parallel lines was obtained given by

$$C = A - 0.60(\delta_{Sty} - \delta_{liq})^2 \qquad (2)$$

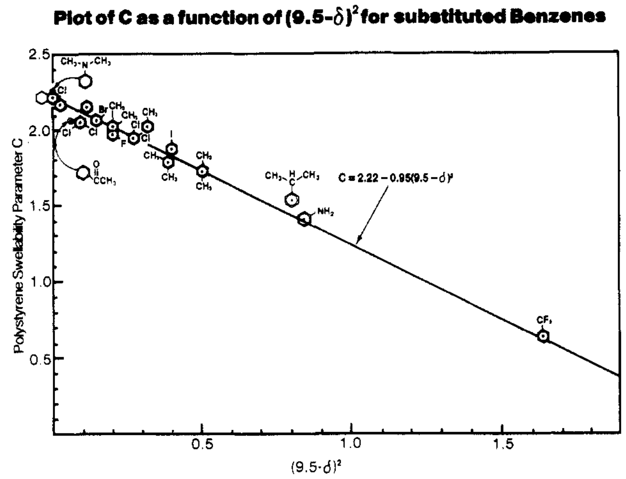

Figure 2. Correlation of observed relative swelling power for poly(Sty-*co*-DVB) with the corresponding $(.95 - \delta_{\text{liq}})^2$, where 9.5 is the observed solubility parameter of the polymer with respect to substituted benzenes; i.e., $\delta_{\text{Sty}} = \delta_{\text{liq}}$ at maximal swelling (Figure 1).

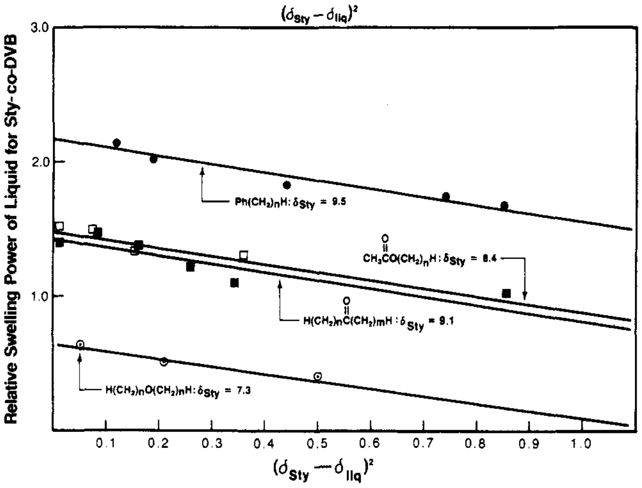

Figure 3. Correlation of relative swelling power for poly(Sty-*co*-DVB) with the corresponding $(\delta_{\text{Sty}} - \delta_{\text{liq}})^2$, where δ_{Sty} is the observed solubility parameter of the polymer with respect to the class of liquids indicated (Table II), i.e., 9.5 for substituted benzenes, 8.4 for aliphatic esters, 9.1 for aliphatic ketones, and 7.3 for aliphatic ethers.

where A was 2.19 for $Ph(CH_2)_nH$, 1.48 for the esters, 1.42 for the ketones, and 0.64 for the ethers (Figure 3).

The observed constants A in eq 2 for these homologous series appear to be a measure of the force of attraction between the functional group of the liquid molecule (i.e., Ph > CO_2 > C=O > O) and the phenyl group of polystyrene. This force of attraction is mitigated by the $(CH_2)_nH$ chain attached to the functional group, apparently in accord with the sum of the CH_2 parachors[14] as explained by Scatchard[15] and Small,[16] which depends on additive enthalpy contributions in accordance with Hildebrand's definition of cohesive energy density.[5]

The contribution to relative swelling power owing to the affinity of a functional group Z in the solvent for the functional group Ph in the solute appears to be additive. Thus, a plot of C for the chlorocarbons of Table II as a function of the corresponding $(\delta_{\text{Sty}} - \delta_{\text{liq}})^2$ does not give a single line parallel to the lines shown in Figure 3. Instead, the data points lie in a broad band demarcated by two imaginary lines as defined by eq 2, where A = 2.4 and 1.2. The swelling power of the dicarbon molecules appears to increase monotonically with the number of chlorine atoms contained therein; i.e., the relative swelling powers C for CH_3CHCl_2, $ClCH_2CH_2Cl$, $ClCH_2CH_2Cl_2$, and Cl_2CH_2-CH_2Cl_2 are 1.68, 1.79, 2.04, and 2.29, respectively. The characteristic constants C for CH_2Cl_2 and $CHCl_3$ are 1.99 and 2.32, respectively, but that for CCl_4 is only 1.97, which may be attributed to the symmetry of perchlorinated carbon or to a decrease in acid strength. Further discussion of relative swelling power exhibited by chlorine-containing liquids will be deferred until we have had time to accumulate swelling data for a much larger number of such liquids.

The effect of substituent R on the relative swelling power of liquid substituted benzenes, RPh, with respect to poly(Sty-*co*-DVB) is evidenced by the data reported in Table I and also by the data reported for the aromatic liquids listed in Table 1 of ref 2. These are summarized as follows: R = $N(CH_3)_2$, C = 2.32; R = Cl, C = 2.18; R = H, C = 2.14; R = Br, C = 2.06; R = CH_3, C = 2.02; R = OCH_3, C = 2.00, R = F, C = 1.98; R = I, C = 1.88, R = NO_2, C = 1.57; R = CF_3, C = 0.71.

Apparently, the electronic contribution by R to the π-electrons of the phenyl group of the liquid, which determines affinity for the phenyl rings of the polymer, is mitigated by the concomitant contribution to molecular size, which determines the magnitude of steric hindrance to accommodation with the polymer.

Ever since Hildebrand pointed out that the cohesive energy density, $\delta^2 = \Delta E/V$ where ΔE is the internal energy and V is the molar volume of the compound in question, is a good criterion for estimating mutual solubility when entropy factors are not important, others have attempted to extend this observation to all solute–solvent systems, even when the entropy factors are very important. This desire for universal applicability has led to a three-dimensional empirical relationship[7-10,12-15] given by

$$\delta_t^2 = \delta_{np}^2 + \delta_p^2 + \delta_h^2$$

where δ_{np} refers to the contribution by nonpolar London dispersion forces (as considered by Hildebrand), δ_p refers to the contribution by dipole–dipole and dipole-induced-dipole forces, and δ_h refers to the contribution by hydrogen-bonding forces. These empirical relationships are complicated to use, and, at best, offer only a qualitative guess with respect to solubility of a given solute in a given solvent.

It was inferred from the results observed in this correlation of swelling power with the corresponding reported solvent parameters that the major contributing factor to solubility of a polymer in a given liquid is the affinity of the functional group, Z, of the liquid for the functional group Ph in the polymer. It follows, therefore, that it may be advantageous to characterize this affinity of Z for Ph in terms of donor–acceptor relationships, as described by Gutman[17] and Drago[18,19] and to apply this to polymer–solvent relationships, as suggested by Fowkes.[20] The mitigating effect on solvent power caused by systematic modification of substituents attached to the functional groups of the solvent and polymeric solute should provide a better understanding of solubility in terms of the molecular structure of the solvent and solute. Such studies should identify solvent–solute systems where entropic considerations and/or mutually attractive sites outweigh the enthalpy contribution to free energy of solution, which presumably is a major reason why the principles of additive cohesive energy density do not explain adequately the solubility results observed for polymer–solvent systems.

Accordingly, I have decided to undertake studies of the relative swelling powers exhibited by liquids in homologous series given by $Z(CH_2)_nH$ with respect to sets of cross-linked polymers of a given molecular type. It is hoped that this will lead to a better understanding of solubility in terms of the molecular structure of the polymeric solute and the liquid. The results of such studies will be reported in subsequent publications.

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

References and Notes

(1) Errede, L. A.; Stoesz, J. D.; Sirvio, L. M. *J. Appl. Polym. Sci.*, in press.

(2) Errede, L. A. *J. Appl. Polym. Sci.*, in press. Presented in part before the Society of Polymer Science, Japan, May 1985 (*Polym. Prepr. Jpn.* **1985**, *34*(1), 9), and in part before the American Chemical Society, Sept 1985 (*Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1985**, *26*(2), 77).

(3) Errede, L. A.; Newmark, R. A.; Hill, J. R. *Macromolecules* **1986**, *19*, 651. Errede, L. A. *Macromolecules* **1986**, *19*, 654.

(4) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.

(5) Hildebrand, J. H.; Scott, R. L. *The Solubility of Non-Electrolytes*, 3rd ed.; Reinhold: New York, 1950.

(6) Gee, G. *Trans. Faraday Soc.* **1946**, *42*, 585.

(7) Hoy, K. L. *Paint Technol.* **1970**, *42*(541), 76. Hoy, K. L. *Tables of Solubility Parameters*, 1975, a bulletin published by Union Carbide Corp.

(8) *A Three Dimensional Approach to Solubility*, a bulletin published by Eastman Co.

(9) Hansen, C. M.; Skaarup, K. J. *Paint Technol. Mol.* **1976**, *39*, 505.

(10) Barton, A. F. F. *Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC: Boca Raton, FL, 1983.

(11) Boyer, R. F.; Spencer, R. S. *J. Polym. Sci.* **1948**, *3*, 97.

(12) Magat, M. J. *Chem. Phys.* **1949**, *46*, 344.

(13) Scott, R. L.; Magat, M. *J. Polym. Sci.* **1949**, *4*, 555.

(14) Van Krevelen, D. W.; Hoftyzer, P. J. *Properties of Polymers*; Elsevier: New York, 1976; 130.

(15) Scatchard, G. *Chem. Rev.* **1945**, *44*, 7.

(16) Small, P. A. *J. Appl. Chem.* **1949**, *3*, 71.

(17) Gutman, V. *The Donor–Acceptor Approach to Molecular Interactions*; Plenum: New York, 1978.

(18) Drago, R. S.; Vogel, G. C.; Needham, T. E. *J. Am. Chem. Soc.* **1971**, *93*, 6014.

(19) Drago, R. S.; Parr, L. B.; Chamberlain, C. S. *J. Am. Chem. Soc.* **1977**, *99*, 3203.

(20) Fowkes, F. W.; Tischler, P. O.; Wolfe, J. A.; Lannigan, L. A.; Ademu-John, C. M.; Halliwell, M. J. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 547.

Polymer Swelling. 6. A Study of Poly(styrene-*co*-divinylbenzene) Swelling in Liquids of the Homologous Series $Ph(CH_2)_nH$

L. A. Errede

3M Science Research Laboratories of Central Research, 3M Center, Building 201-2N-22, St. Paul, Minnesota 55144. Received October 17, 1985

ABSTRACT: It is shown that the relative swelling power, C, for styrene-*co*-divinylbenzene polymers exhibited by liquids in the homologous series $Ph(CH_2)_nH$ decreases monotonically with n from $n = 0$ to $n = 10$; the relationship of C in terms of n for the first five members of the homologous series is given by $C = 2.10 - 0.108n$. Thereafter, C deviates negatively from this line by an amount Δ given approximately by $\Delta = 0.07m$, where $m = n - 6$ for all $n > 5$ and also by $\Delta = 0.04F_{cmo}^2 + 0.06F_{cmo} + 0.02$, where $F_{cmo} = 1.15m^{1/2} - 0.81$ is the force of correlated molecular orientation measured by others for association of liquids in the homologous series $H(CH_2)_nH$. A similar pattern is exhibited in the correlation of C with δ, the Hildebrand solubility parameter; i.e., C is a linear function of $(9.5 - \delta_{liq})^2$ for liquids $Ph(CH_2)_{n<7}H$, but it deviates negatively from the line $C = 2.19 - 0.60(9.5 - \delta_{liq})^2$ by an amount $d = 0.33F_{cmo}$ for liquids $Ph(CH_2)_{n>6}H$.

Introduction

We reported[1-3] that the swellability, S, of styrene-*co*-divinylbenzene polymers at equilibrium with excess liquid is related to the average number of atoms, λ, in the backbone of the polystyrene segments between cross-link junctions by the equation

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

where C is the swellability consant of the liquid with respect to Sty-*co*-DVB and λ_0^{-1} is the critical cross-link density of the polymer above which $S = 0$. Correlation of C with the corresponding Hildebrand solubility parameter, δ, of the swelling liquids[4] showed that δ_{Sty} determined thereby depends on the class of liquids used to make such correlations. Thus, $\delta_{Sty} = 9.5$ for substituted benzenes, 9.2 for chlorocarbons, 9.1 for ketones, 8.4 for esters, and 7.3 for ethers. When C was correlated with the corresponding $(\delta_{Sty} - \delta_{liq})^2$ for the lower members of the homologous series $Z(CH_2)_nH$, a set of parallel lines was obtained given approximately by the general equation

$$C = A - 0.60(\delta_{Sty} - \delta_{liq})^2 \qquad (2)$$

where A was 2.19 for Z = Ph, 1.48 for esters, 1.42 for ketones, and 0.64 for ethers.[4]

This implies that the major factor that determines swelling and/or solvent power of a given liquid for Sty-*co*-DVB polymers is the affinity of the functional group Z of that liquid for the polymer components, especially the pendant phenyl group,[4] and that the $(CH_2)_nH$ attached to Z mitigates this affinity in accordance with the additive contribution of each CH_2 group as suggested by Scatchard[5] and Small.[6]

It was of interest, therefore, to see if eq 2, which was observed to be applicable for the lower members of the homologous series $Z(CH_2)_nH$, i.e., for $n < 5$, is also valid for the higher members of these series, i.e., for $n > 5$. To this end I decided to study first the relationship of C as a function of n, from 0 to 10, for liquids in the homologous series $Ph(CH_2)_nH$ and then to correlate C with $(9.5 - \delta)^2$, where δ_n is the solubility parameter of the nth member of the homologous series. The purpose of this publication is to report the results of that study.

General Procedure

The test liquids listed in Table I were obtained from commercial sources, mostly from Aldrich Chemical Co., and were used without further purification. The Sty-*co*-DVB polymers made to undergo swelling in these liquids were obtained from Bio-Rad Laboratories. Aliquots of these polymers in the form of microbeads (the DVB

0024-9297/86/2219-1525$01.50/0