5 Methods of Characterization — Polymers

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ABSTRACT

The simplest experimental method to determine the Hansen solubility parameters (HSP) for a polymer is to evaluate whether or not it dissolves in selected solvents. Those solvents dissolving the polymer will have HSP closer to those of the polymer than those solvents that do not. A computer program or graphical method can then be used to find the HSP for the polymer. Other types of evaluations can also lead to polymer HSP. These include swelling, melting point reduction, surface attack, chemical resistance, barrier properties, viscosity measurements, and any other measurement reflecting differences in polymer affinities among the solvents.

Polymer HSP can be higher than the HSP of any of the test solvents. This means that some of the methods suggested in the literature to interpret data, i.e., those which use averages of solvent HSP to arrive at the polymer HSP, must be used with care.

INTRODUCTION

Experience has shown that if it is at all possible, an experimental evaluation of the behavior of a polymer in contact with a series of selected liquids is the best way to arrive at its HSP. Experimental data can be generated and treated in various ways to arrive at the values of interest. Examples are included in the following.

The author's usual approach to generate data in solubility parameter studies is to contact a polymer of interest with 40 to 45 well-chosen liquids. One may then observe or measure a number of different phenomena including full solution at a given concentration, degree of swelling by visual observation or by measurement of weight change, volume change, clarity, surface attack, etc. The object of the studies is to determine differences in affinity of the polymer for the different solvents. These differences are then traditionally used to divide the solvents into two groups, one which is considered "good" and the other which is considered "bad." Such data can be entered into the SPHERE program as discussed in Chapter 1. Whenever possible, the author uses a set of solvents as described below, often supplemented by selected solvents depending on the purpose of the investigation. Supplementary test solvents are usually in the boundary regions as it is these that determine the parameters of the sphere. Adding more good solvents well within the sphere or more bad solvents well outside of it will not change anything but the data fit.

The goal of the experimental work is to arrive at a set of data showing differences in behavior among the test solvents. These data are then processed to arrive at the four parameters characteristic of HSP correlations, three describing the nonpolar, polar, and hydrogen-bonding interactions for the liquids and the fourth, Ro, a radius of interaction for the type of interaction described.

The author has most often used computer techniques to evaluate the data to find the polymer HSP. In earlier work simple plots were used. A simple plot of δ_P vs. δ_H is also helpful in many practical situations to get guidance as discussed in Chapter 8. The approximate determination of polymer HSP can be done with three plots of experimental data using the HSP parameters pairwise. Figure 5.1 to Figure 5.3 demonstrate how this was attempted initially.[1] The spheroids in the figures including the δ_D parameter gave problems. Hansen and Skaarup[2] simply used a scaling factor of 2 (the coefficient "4" in Chapter 1, Equation 1.9) to produce spheres in all three plots. As Ro must
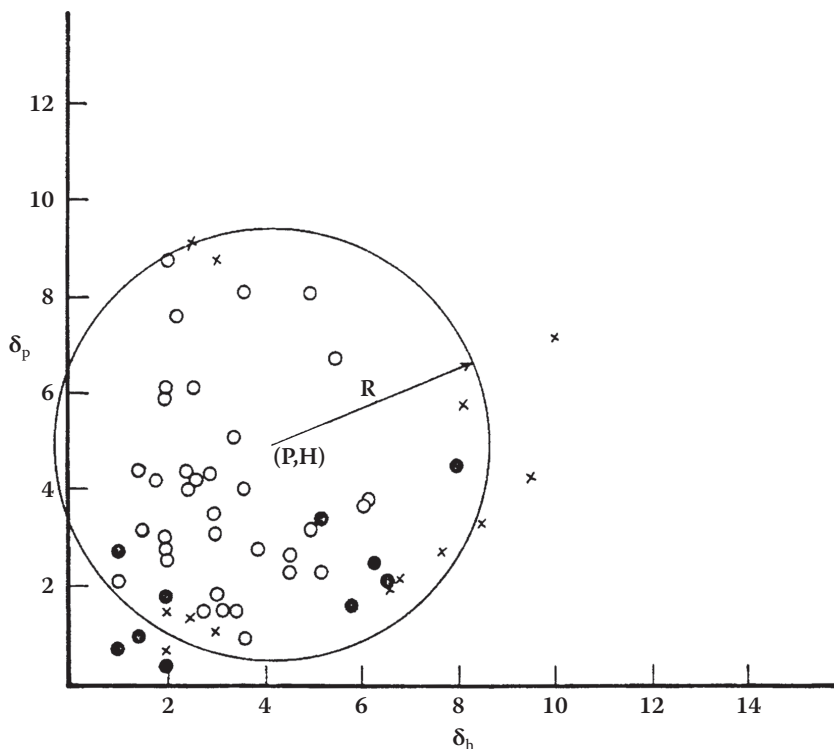
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FIGURE 5.1 Two-dimensional plot of δ_P vs. δ_H for the solubility of polymethyl methacrylate (Polymer B in Table 5.2). The circle is the projection of a sphere on the given coordinates. Units are $(cal/cm^3)^{1/2}$. (From Hansen, C.M., *Färg och Lack*, 17(4), 71, 1971. With permission.)

be the same in all of these plots, a single compass setting is tried for a set of δ_D, δ_P, and δ_H to see how well the separation into good and bad solvents is accomplished. Calculations for points in doubt can be made using Chapter 1, Equation 1.9. Plots with the modified δ_D axis are given for the solubility of polystyrene[3] shown in Figure 5.4 to Figure 5.6. These are the original figures from this thesis, and the numbers refer to a table of solvents found there. An idea of the accuracy of the graphical approach can be found in Table 5.1, where comparisons are made between the "hand" method and results of the SPHERE program. Table 5.2 contains a listing of the polymers included in Table 5.1. Specific solubility data are given for these polymers in 88 solvents in Appendix A.3.

Teas[4] has developed a triangular plotting technique which helps visualization of three parameters on a plain sheet of paper. Examples are found in Reference 5 to Reference 7 and in Chapter 8. The triangular plotting technique uses parameters for the solvents, which, in fact, are modified HSP parameters. The individual Hansen parameters are normalized by the sum of the three parameters. This gives three fractional parameters defined by Equation 5.1 to Equation 5.3.

$$f_d = 100\delta_D/(\delta_D + \delta_P + \delta_H) \tag{5.1}$$

$$f_P = 100\delta_P/(\delta_D + \delta_P + \delta_H) \tag{5.2}$$

$$f_h = 100\delta_H/(\delta_D + \delta_P + \delta_H) \tag{5.3}$$

The sum of these three fractional parameters is 1.0. This allows the use of the special triangular technique. Some accuracy is lost, and there is no theoretical justification for this plotting technique,
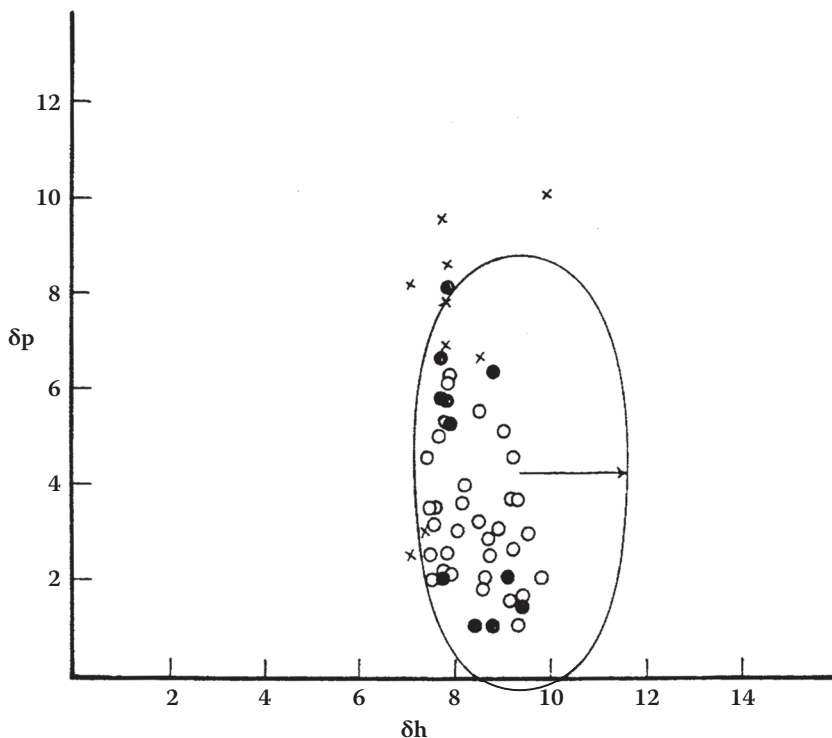
FIGURE 5.2 Two-dimensional plot of δ_H vs. δ_D for the solubility of polymethyl methacrylate (Polymer B in Table 5.2). Expansion of the δ_D scale by a factor of 2 would yield a circle (a sphere in projection). Units are $(cal/cm^3)^{1/2}$. (From Hansen, C.M., *Färg och Lack*, 17(4), 71, 1971. With permission.)

but one does get all three parameters onto a two-dimensional plot. This plotting technique is often used by those who conserve old paintings, because it was described in a standard reference book very shortly after it was developed.[7] Figure 8.4 shows how such a plot can be used in finding a suitable solvent when dealing with such an older oil painting.

HSP for the polymers and film formers discussed in the following examples are given in Table 5.3. These data are based on solubility determinations unless otherwise noted. Barton[6,8] has also provided solubility parameters for many polymers. Values for a number of acrylic, epoxy, and other polymers potentially useful in self-stratifying coatings have been reported by Benjamin et al.[9] (see Chapter 8). Rasmussen and Wahlström[10] provide additional HSP data in relation to the use of replenishable natural products (oils) in connection with solvents. The data processing techniques and data accumulated by Zellers and coworkers[11–14] on elastomers used in chemical protective clothing are also useful. Zellers et al. also point out many of the problems encountered with these characterizations. Such problems are also discussed below. There are other sources of HSP for polymers in the literature, but a full review of these and their uses is beyond the scope of this book.

CALCULATION OF POLYMER HSP

Calculation of the HSP for polymers is also possible. The results are not yet fully satisfactory, but there is hope for the future. One of the more significant efforts in this has been made by Utracki and coworkers.[15,16] They assumed the δ_D parameter for polymers did not differ too much between polymers and interpreted evaluations of polymer–polymer compatibility using calculated values for δ_P and δ_H. A word of caution is advisable here and that is that the constant "4" in Equation 1.9 is very often if not most often significant, and should not be replaced with a "1," either. Group
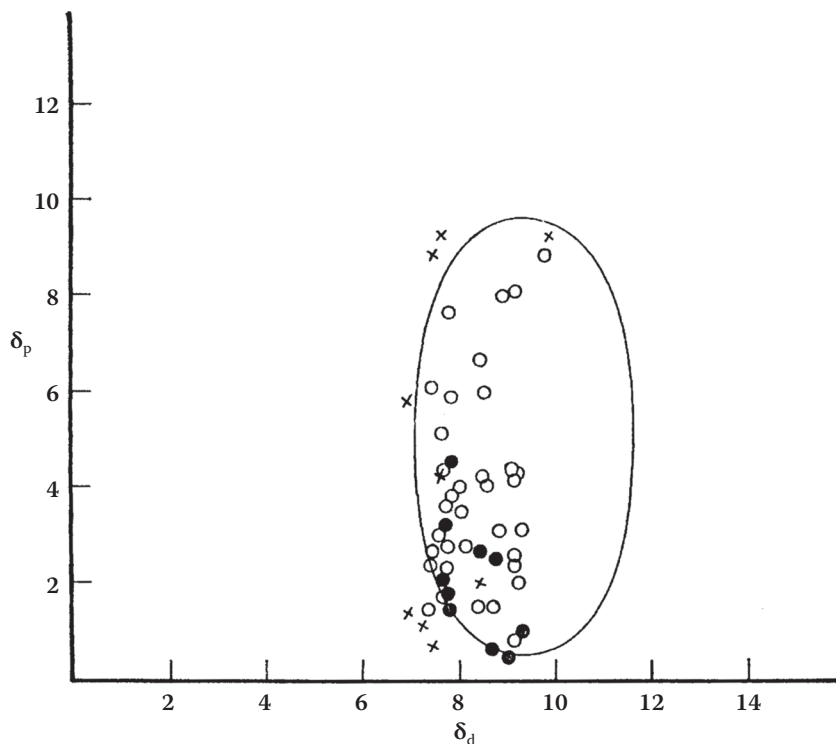
FIGURE 5.3 Two-dimensional plot of δ_P vs. δ_D for the solubility of polymethyl methacrylate (Polymer B in Table 5.2). Expansion of the δ_D scale by a factor of 2 would yield a circle (a sphere in projection). Units are (cal/cm³)¹ᐟ². (From Hansen, C.M., *Färg och Lack*, 17(4), 72, 1971. With permission.)

calculations were used. This is probably the best calculation approach currently available, but improvements are thought possible. See Chapter 3. The group contributions given in Chapter 1 can be used for this purpose, although the estimated dispersion parameters are thought to be too low. It is suggested that HSP for polymers determined by these calculations not be mixed with experimentally determined HSP until confirmation of agreement is found. It can be presumed that the errors involved in either process will cancel internally, but these may not necessarily be the same for the calculated results as for the experimental ones.

The author has never been particularly successful in calculating the same values as were found experimentally, although a serious effort to use weighting and similar factors, as discussed in the following, has never been tried.

SOLUBILITY — EXAMPLES

The most direct method to determine the three HSP for polymers or other soluble materials is to evaluate their solubility or degree of swelling/uptake in a series of well-defined solvents. The solvents should have different HSP chosen for systematic exploration of the three parameters at all levels. As indicated earlier, a starting point could be the series of liquids used by the author for many years. These are essentially those included in Table 5.4. Sometimes boundaries are defined better by inclusion of additional test solvents. A computer analysis quickly gives a choice of many of these, as solvents with RED numbers (Chapter 1, Equation 1.10) near 1.0 are located near the sphere boundary. It is actually the boundary which is used to define the center point of the sphere using Chapter 1, Equation 1.9. Some changes are also possible to remove or replace solvents which are now considered too hazardous, although good laboratory practice should allow use of the ones
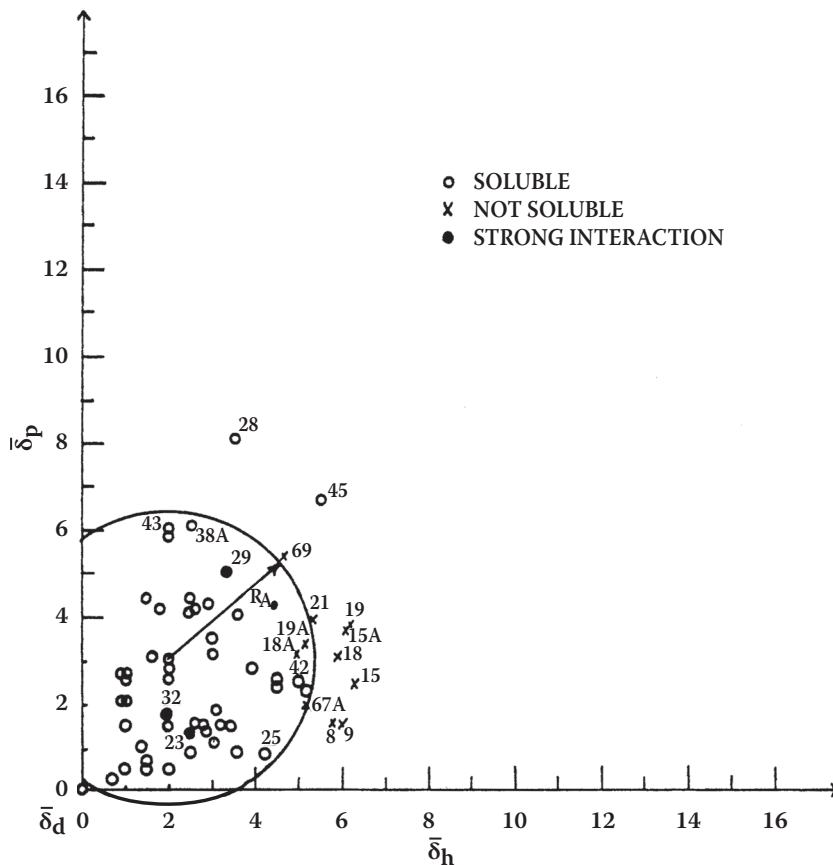
FIGURE 5.4 Two-dimensional plot δ_P vs. δ_H of solubility data for polystyrene (Polymer G in Table 5.2). Units are $(cal/cm^3)^{1/2}$.

indicated. The HSP generally in use for liquids have all been evaluated/calculated at 25°C. These same values can also be used to correlate physical phenomena related to solubility at other test temperatures with some care, as noted in the following.

Several examples of HSP correlations based on solubility are found in Table 5.3. The entry for polyethersulfone (PES) found in Table 5.3 was determined from data included in the computer output reported in Table 5.4. The solubility of PES was evaluated in 41 different solvents. It was found that five of them actually dissolved the polymer. The input data to the SPHERE program described in Chapter 1 are included in Table 5.4 in the SOLUB column. A "1" means a good solvent and a "0" means a bad solvent. A 1* means that a good solvent lies outside the sphere, where it should not, and a 0* means a bad solvent lies inside the sphere, which means it is an outlier. Each of these error situations reduces the data fit. D, P, H, and R for the solubility of PES are given at the top. In addition, there is an indication of the data fit, which is 0.999 here. A perfect fit is 1.000. A data fit slightly less than 1.0 is actually preferred, as the computer program has then optimized the data to a single set of values that are so close to being correct as they can be within experimental error. An unknown number of sets of the parameters can give a data fit of 1.0 whenever this result is found. Perfect fits are rather easily obtained with small sets of data, and the boundaries are rather poorly defined, which means the center is also poorly defined. One can continue testing with additional solvents located in the boundary regions of the established sphere as stated previously. These can be found easily by listing the solvents in order of their RED numbers and choosing
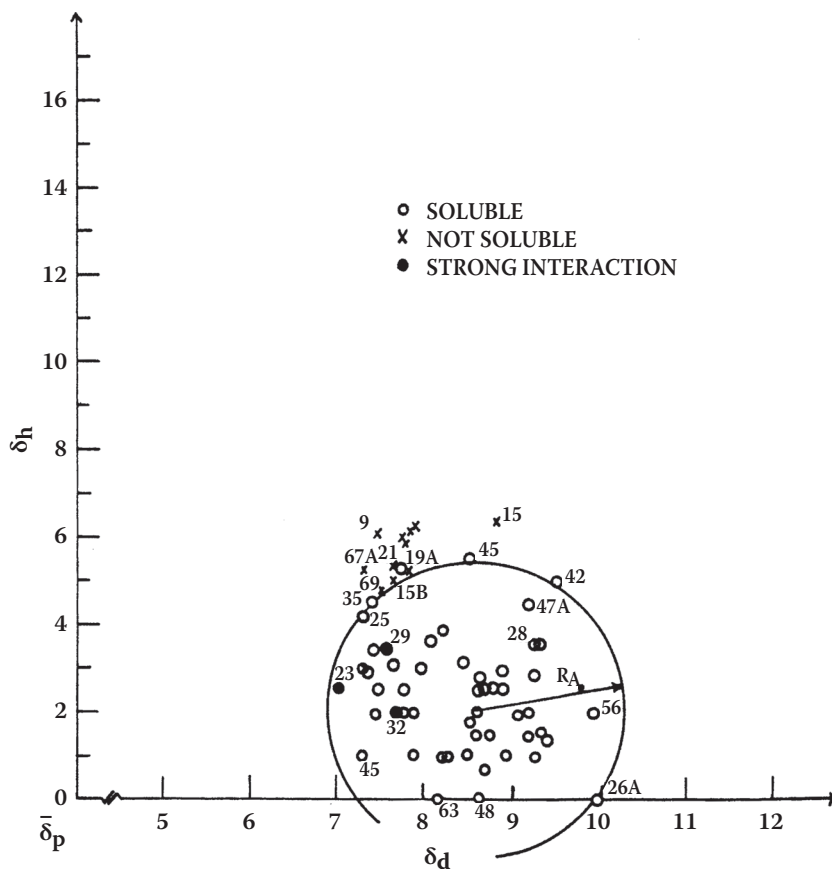
FIGURE 5.5 Two-dimensional plot δ_H vs. δ_D of solubility data for polystyrene (Polymer G in Table 5.2). Expansion of the δ_D scale by a factor of 2 has given a spherical representation according to Chapter 1, Equation 1.9. Units are $(cal/cm^3)^{1/2}$.

those with values not too different from 1.0. The RED number is given for each solvent in the RED column. A quality number, Q = 1 − RED, is also conceptually useful.

Finally, there is a column in Table 5.4 indicating the molar volume, V, of the solvents in cc/mol. There was no need to analyze the influence of this parameter in the present case.

A second example of this type of approach is given in Table 5.3. Data on good and bad solvents[17] for polyacrylonitrile (PAN) have been used as input to the computer program. There are 13 solvents indicated as good, and 23 indicated as bad. These test solvents do not differ as widely from each other as the test series suggested earlier, but the data are still useful in finding the HSP for this polymer. These are reported in Table 5.3. The data fit of 0.931 is good for this kind of data. Having found the HSP for a polymer in this manner, one can then search a database for additional solvents for the polymer in question. This was done for the HSP database with over 800 solvent entries in Table A.1 of the first edition of this handbook. A significantly large number of the 123 additional solvents found to have RED numbers less than 1.0 can be expected to dissolve this polymer, but such an extensive experimental study was not undertaken to confirm the predictions.

A special problem that can be encountered is when only a few solvents with very high solubility parameters dissolve a polymer. An example is polyvinyl alcohol with true solvents being 1-propanol and ethanol in a data set with 56 solvents.[6] The entry in Table 5.3 places a big question mark over the solubility parameters, as well as with the radius 4.0 and the perfect fit of the data. The computer analysis quickly encompasses the two good solvents in the data set within a small sphere as they
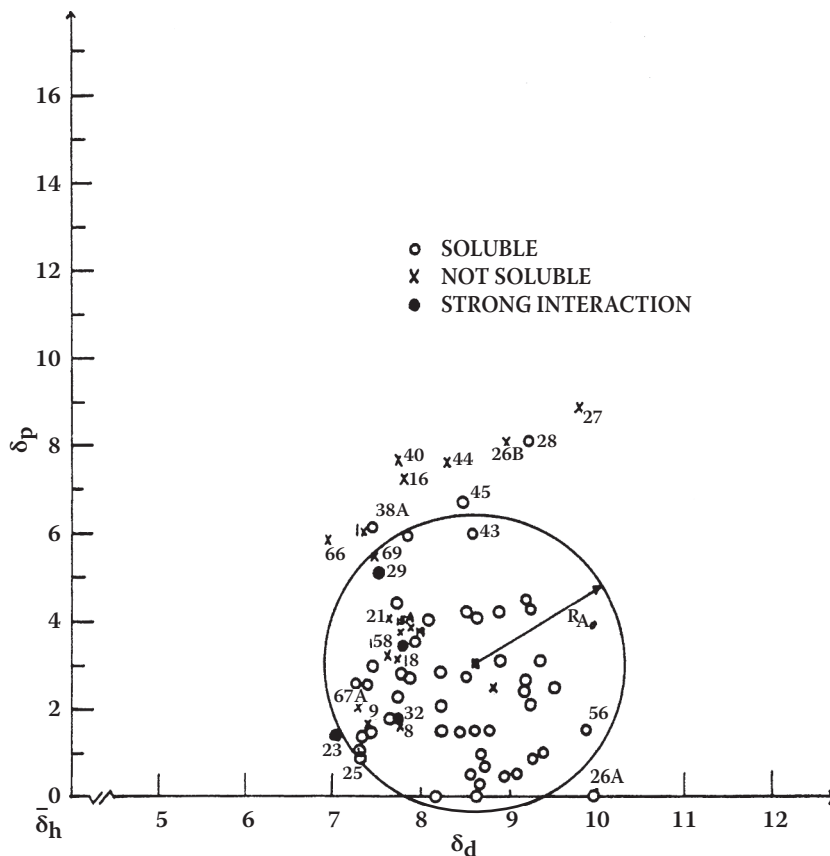
FIGURE 5.6 Two-dimensional plot δ_P vs. δ_D of solubility data for polystyrene (Polymer G in Table 5.2). Expansion of the δ_D scale by a factor of 2 has given a spherical representation according to Chapter 1, Equation 1.9. Units are $(cal/cm^3)^{1/2}$.

have reasonably similar parameters. Based on reasonable similarity with other solubility correlations for water-soluble polymers, one anticipates spheres with a radius much larger than the distance between these solvents. This result is not good and should not be used.

Another example of determining HSP for a polymer with very high solubility parameters is Dextran C (British Drug Houses). Only 5 out of 50 solvents were found to dissolve Dextran C.[18] In this case, there was enough spread in the solubility parameters of the test solvents such that the spherical model correlation (Chapter 1, Equation 1.9) forced the program to find a radius of 17.4 $MPa^{1/2}$. This appears to be a reasonable number for this situation. The problem can be made clearer by noting the dissolving solvents with their RED numbers in parentheses. These were dimethyl sulfoxide (1.000), ethanolamine (0.880), ethylene glycol (0.880), formamide (0.915), and glycerol (0.991). Some dissolving liquids had RED equal to 1.0 or higher and included diethylene glycol (1.000), propylene glycol (1.053), and 1,3-butanediol (1.054). These helped to define the boundary of the Hansen solubility sphere. Note that the HSP for the polymer are in a region higher than that defined by the values of test liquids. Any technique using an average of the HSP for the test solvents will inherently underestimate the solute HSP in such a situation. The solubility data for the polymer Dextran C led to the HSP data reported in Table 5.3 when the SPHERE program used a starting point based on averages of the HSP values for the good solvents. When the starting point was 25 $MPa^{1/2}$ for D, P, H, and Ro, respectively, a perfect data fit was found for D, P, H, and Ro equal to 26, 26, 26, and 24, all in $MPa^{1/2}$. When the starting point was for D, P, H, and Ro equal to 30, 30,

TABLE 5.1
Calculated vs. Trial-and-Error Solubility Parameter Data for Various Polymers[a]

Computed Handtrials	(First Values) (Second Values)					Computed Handtrials	(First Values) (Second Values)				
	δ_D	δ_P	δ_H	Ro	FIT		δ_D	δ_P	δ_H	Ro	FIT
A	8.60	4.72	1.94	5.20	0.960	R	9.04	4.50	2.40	5.20	0.985
	9.2	5.3	2.1	5.3	0.923		9.2	4.5	2.6	5.0	0.972
B	9.11	5.14	3.67	4.20	0.945	S	10.53	7.30	6.00	8.20	0.910
	9.2	5.0	4.2	4.0	0.923		8.8	7.0	5.5	6.0	0.879
C	9.95	5.88	5.61	6.20	0.853	T	8.58	1.64	1.32	3.20	0.974
	8.5	5.5	5.5	4.7	0.829		8.7	1.8	1.8	3.5	0.965
D	9.98	1.68	2.23	6.70	0.974	U	9.10	4.29	2.04	4.70	0.969
	8.5	2.5	3.0	5.3	0.957		9.3	4.5	2.0	4.7	0.950
E	9.79	2.84	5.34	5.70	0.930	V	8.10	0.69	–0.40	4.70	0.974
	9.4	3.2	5.1	5.0	0.929		8.5	1.5	1.5	3.4	0.964
F	9.09	2.13	6.37	5.20	0.948	X	7.10	1.23	2.28	6.20	0.921
	8.5	4.3	5.5	4.8	0.871		7.8	1.0	3.6	4.0	0.881
G	10.40	2.81	2.10	6.20	0.955	Y	8.57	1.10	1.67	3.20	0.950
	8.6	3.0	2.0	3.5	0.915		8.8	2.5	1.2	3.8	0.914
H	10.23	5.51	4.72	6.70	0.891	Z	8.52	–0.94	7.28	4.70	0.971
	9.3	5.0	4.0	4.9	0.855		8.2	0.8	5.7	2.9	0.954
I	10.17	4.05	7.31	6.20	0.924	A	9.60	2.31	3.80	5.20	0.942
	9.5	4.0	6.4	4.7	0.909		8.7	2.5	3.5	4.2	0.951
J	7.53	7.20	4.32	5.60	0.933	B	9.95	4.17	5.20	7.20	0.980
	7.0	7.0	4.3	5.5	0.918		9.5	4.0	5.5	7.0	0.976
K	9.90	3.09	2.64	5.20	0.949	C	8.05	0.18	1.39	4.20	0.966
	9.3	3.7	2.1	4.2	0.933		8.5	1.0	2.0	3.4	0.960
L	9.08	6.22	5.38	3.70	0.921	D	10.34	6.63	6.26	6.70	0.964
	9.5	6.0	6.0	4.5	0.896		9.2	5.8	4.2	5.0	0.868
M	11.37	3.20	4.08	9.70	0.978	E	8.58	0.58	1.76	3.20	0.968
	9.0	4.0	5.5	6.4	0.923		8.5	1.5	1.8	2.6	0.956
N	9.65	5.68	7.13	6.20	0.897	F	8.91	3.68	4.08	1.70	0.992
	9.4	5.3	7.4	5.5	0.867		9.4	4.5	3.5	3.2	0.895
O	10.62	0.46	4.17	7.70	1.000	G	9.49	2.68	2.82	4.70	0.961
	8.9	3.0	3.8	4.5	0.952		8.8	2.7	2.7	4.0	0.963
P	8.58	4.58	7.00	5.20	0.942	L	9.86	7.14	7.35	5.70	0.970
	8.5	4.7	6.5	5.0	0.940		10.8	7.0	8.8	7.1	0.936
Q	9.87	6.43	6.39	5.70	0.942		9.3	6.2	4.7	4.2	0.892

Note: Units are (cal/cm³)^1/2.

[a] See Table 5.2 for polymer types.

Source: From Hansen, C.M., *Färg och Lack*, 17(4), 73, 1971. With permission.

30, and 30, all in MPa^1/2, a perfect correlation was found to D, P, H, and Ro equal to 30, 28, 28, and 32, all in MPa^1/2. These data show that extrapolations into regions where there are no data can be problematic. It is thought that the data given in Table 5.3 for Dectran C are the most representative, because of the data fit being slightly less than 1.0 giving a better definition of a boundary.

The properties of good solvents alone cannot always lead to a good estimate of the solubility parameters for these polymers, and the radii of spheres using only a few solvents with high solubility parameters will be very uncertain. One can sometimes find better results by correlating degrees of swelling or uptake, rather than correlate on solubility or not. The work of Zellers and coworkers

TABLE 5.2
List of Polymers and Resins Studied

A   Lucite® 2042-poly (ethyl methacrylate), E. I. du Pont de Nemours & Co., Inc.

B   Poly (methyl methacrylate), Rohm and Haas Co.

C   Epikote® 1001-epoxy, Shell Chemical Co.

D   Plexal P65-66% oil length alkyd, Polyplex.

E   Pentalyn® 830-alcohol soluble rosin resin, Hercules Incorporated.

F   Butvar® B76-poly (vinyl butyral), Shawinigan Resins Co.

G   Polystyrene LG, Badische Anilin- und Soda Fabrik.

H   Mowilith® 50-poly (vinyl acetate), Farbwerke Hoechst.

I   Plastopal H-urea formaldehyde resin, Badische Anilin- und Soda Fabrik.

J   H Sec. Nitrocellulose-H 23, A. Hagedorn and Co.

K   Parlon® P10-chlorinated poly (propylene), Hercules Incorporated.

L   Cellulose acetate, Cellidora A-Bayer AG.

M   Super Beckacite® 1001-Pure Phenolic Resin, Reichhold Chemicals Co.

N   Phenodur 373U-phenol-resol resin, Chemische Werke Albert.

O   Cellolyn 102-modified pentaerythritol ester of rosin, Hercules Incorporated.

P   Pentalyn 255-alcohol soluble resin, Hercules Incorporated.

Q   Suprasec F5100-blocked isocyanate (phenol), Imperial Chemical Ind. Ltd.

R   Plexal C34-34% coconut oil-phthalic anhydride alkyd, Polyplex.

S   Desmophen 850, Polyester-Farbenfabriken Bayer AG.

T   Polysar 5630 — styrene-butadiene (SBR) raw elastomer, Polymer Corp.

U   Hycar® 1052-acrylonitrile-butadiene raw elastomer, B. F. Goodrich Chemical Corp.

V   Cariflex IR 305-isoprene raw elastomer, Shell Chemical Co.

X   Lutanol IC/123-poly (isobutylene), Badische Anilin- und Soda Fabrik.

Y   Buna Huls CB 10-cis poly butadiene raw elastomer, Chemische Werke Huels.

Z   Versamid® 930-polyamide, General Mills, Inc.

A   Ester gum BL, Hercules Incorporated.

B   Cymel® 300-hexamethoxy melamine, American Cyanamid Co.

C   Piccolyte® S100-terpene resin, Pennsylvania Industrial Chemical Corp.

D   Durez® 14383-furfuryl alcohol resin, Hooker Chemical Co.

E   Piccopale® 110-petroleum hydrocarbon resin, Pennsylvania Industrial Chemical Corp.

F   Vipla KR-poly (vinyl chloride), K = 50, Montecatini.

G   Piccoumarone 450L-cumarone-indene resin, Pennsylvania Industrial Chemical Corp.

L   Milled wood lignin — special sample from Prof. A. Björkman.

TABLE 5.3
Hansen Solubility Parameter Correlations for Selected Materials

Material	δ_D	δ_P	δ_H	Ro	FIT	G/T
PES solubility	19.6	10.8	9.2	6.2	0.999	5/41
PAN solubility	21.7	14.1	9.1	10.9	0.931	13/36
PP swelling	18.0	3.0	3.0	8.0	1.00	13/21
Polyvinyl alcohol ? (see text)	17.0	9.0	18.0	4.0	1.00	2/56
Hexamethylphosphoramide	18.5	8.6	11.3	—	—	—
PVDC melting temperature 110°C	17.6	9.1	7.8	3.9	0.992	6/24
PVDC melting temperature 130°C	20.4	10.0	10.2	7.6	0.826	13/24
Dextran C solubility	24.3	19.9	22.5	17.4	0.999	5/50

Note: Units are (cal/cm³)$^{1/2}$.

TABLE 5.4A
Calculated Solubility SPHERE for PES Solubility

D = 19.6 P = 10.8 H = 9.2 RAD = 6.2 FIT = 0.999 NO = 41

Solvent	D	P	H	SOLUB	RED	V
Acetone	15.5	10.4	7.0	0	1.371	74.0
Acetophenone	19.6	8.6	3.7	1	0.955	117.4
Benzene	18.4	0.0	2.0	0	2.129	89.4
1-Butanol	16.0	5.7	15.8	0	1.777	91.5
Butyl acetate	15.8	3.7	6.3	0	1.741	132.5
γ-Butyrolactone	19.0	16.6	7.4	1	0.998	76.8
Carbon tetrachloride	17.8	0.0	0.6	0	2.301	97.1
Chlorobenzene	19.0	4.3	2.0	0	1.576	102.1
Chloroform	17.8	3.1	5.7	0	1.483	80.7
Cyclohexanol	17.4	4.1	13.5	0	1.467	106.0
Diacetone alcohol	15.8	8.2	10.8	0	1.321	124.2
o-Dichlorobenzene	19.2	6.3	3.3	0	1.204	112.8
Diethylene glycol	16.6	12.0	20.7	0	2.101	94.9
Diethyl ether	14.5	2.9	5.1	0	2.183	104.8
Dimethyl formamide	17.4	13.7	11.3	1	0.915	77.0
Dimethyl sulfoxide	18.4	16.4	10.2	0*[a]	0.996	71.3
1,4-Dioxane	19.0	1.8	7.4	0	1.493	85.7
Ethanol	15.8	8.8	19.4	0	2.077	58.5
Ethanolamine	17.0	15.5	21.2	0	2.241	59.8
Ethyl acetate	15.8	5.3	7.2	0	1.547	98.5
Ethylene dichloride	19.0	7.4	4.1	0	1.007	79.4
Ethylene glycol	17.0	11.0	26.0	0	2.837	55.8
Ethylene glycol monobutyl ether	16.0	5.1	12.3	0	1.563	131.6
Ethylene glycol monoethyl ether	16.2	9.2	14.3	0	1.395	97.8
Ethylene glycol monomethyl ether	16.2	9.2	16.4	0	1.618	79.1
Formamide	17.2	26.2	19.0	0	3.044	39.8
Hexane	14.9	0.0	0.0	0	2.745	131.6
Isophorone	16.6	8.2	7.4	0	1.094	150.5
Methanol	15.1	12.3	22.3	0	2.575	40.7
Methylene dichloride	18.2	6.3	6.1	1	0.990	63.9
Methyl ethyl ketone	16.0	9.0	5.1	0	1.368	90.1
Methyl isobutyl ketone	15.3	6.1	4.1	0	1.782	125.8
Methyl-2-pyrrolidone	18.0	12.3	7.2	1	0.655	96.5
Nitroethane	16.0	15.5	4.5	0	1.580	71.5
Nitromethane	15.8	18.8	5.1	0	1.899	54.3
2-Nitropropane	16.2	12.1	4.1	0	1.387	86.9
Propylene carbonate	20.0	18.0	4.1	0	1.429	85.0
Propylene glycol	16.8	9.4	23.3	0	2.457	73.6
Tetrahydrofuran	16.8	5.7	8.0	0	1.237	81.7
Toluene	18.0	1.4	2.0	0	1.978	106.8
Trichloroethylene	18.0	3.1	5.3	0	1.485	90.2

Note: Units are MPa$^{1/2}$.

[a] Outlier (a bad solvent lying inside sphere).

ALTERNATE TABLE 5.4B
Calculated Solubility SPHERE for PES Solubility (Listed in RED Order)

D = 19.6 P = 10.8 H = 9.2 RAD = 6.2 FIT = 0.999 NO = 41

Solvent	D	P	H	SOLUB	RED	V
Methyl-2-pyrrolidone	18.0	12.3	7.2	1	0.655	96.5
Dimethyl formamide	17.4	13.7	11.3	1	0.915	77.0
Acetophenone	19.6	8.6	3.7	1	0.955	117.4
Methylene dichloride	18.2	6.3	6.1	1	0.990	63.9
Dimethyl sulfoxide	18.4	16.4	10.2	0*a	0.996	71.3
γ-Butyrolactone	19.0	16.6	7.4	1	0.998	76.8
Ethylene dichloride	19.0	7.4	4.1	0	1.007	79.4
Isophorone	16.6	8.2	7.4	0	1.094	150.5
o-Dichlorobenzene	19.2	6.3	3.3	0	1.204	112.8
Tetrahydrofuran	16.8	5.7	8.0	0	1.237	81.7
Diacetone alcohol	15.8	8.2	10.8	0	1.321	124.2
Methyl ethyl ketone	16.0	9.0	5.1	0	1.368	90.1
Acetone	15.5	10.4	7.0	0	1.371	74.0
2-Nitropropane	16.2	12.1	4.1	0	1.387	86.9
Ethylene glycol monoethyl ether	16.2	9.2	14.3	0	1.395	97.8
Propylene carbonate	20.0	18.0	4.1	0	1.429	85.0
Cyclohexanol	17.4	4.1	13.5	0	1.467	106.0
Chloroform	17.8	3.1	5.7	0	1.483	80.7
Trichloroethylene	18.0	3.1	5.3	0	1.485	90.2
1,4-Dioxane	19.0	1.8	7.4	0	1.493	85.7
Ethyl acetate	15.8	5.3	7.2	0	1.547	98.5
Ethylene glycol monobutyl ether	16.0	5.1	12.3	0	1.563	131.6
Chlorobenzene	19.0	4.3	2.0	0	1.576	102.1
Nitroethane	16.0	15.5	4.5	0	1.580	71.5
Ethylene glycol monomethyl ether	16.2	9.2	16.4	0	1.618	79.1
Butyl acetate	15.8	3.7	6.3	0	1.741	132.5
1-Butanol	16.0	5.7	15.8	0	1.777	91.5
Methyl isobutyl ketone	15.3	6.1	4.1	0	1.782	125.8
Nitromethane	15.8	18.8	5.1	0	1.899	54.3
Toluene	18.0	1.4	2.0	0	1.978	106.8
Ethanol	15.8	8.8	19.4	0	2.077	58.5
Diethylene glycol	16.6	12.0	20.7	0	2.101	94.9
Benzene	18.4	0.0	2.0	0	2.129	89.4
Diethyl ether	14.5	2.9	5.1	0	2.183	104.8
Ethanolamine	17.0	15.5	21.2	0	2.241	59.8
Carbon tetrachloride	17.8	0.0	0.6	0	2.301	97.1
Propylene glycol	16.8	9.4	23.3	0	2.457	73.6
Methanol	15.1	12.3	22.3	0	2.575	40.7
Hexane	14.9	0.0	0.0	0	2.745	131.6
Ethylene glycol	17.0	11.0	26.0	0	2.837	55.8
Formamide	17.2	26.2	19.0	0	3.044	39.8

Note: Units are MPa$^{1/2}$.

[a] Outlier (a bad solvent lying inside sphere).

reports extensive studies of this type.[11–14] It should be noted, however, that the HSP-sphere parameters usually vary some from correlation to correlation based on the same data when different criteria are used for good and bad solvents. This is because the absorbed solvent tends to locate in regions with similar solubility parameters, and there are local variations in HSP within most, if not all, polymers. This is particularly true of polymers which are not homopolymers. This situation relates to self-assembly. Solvents or segments of molecules with similar HSP will tend to reside near each other. An example of this is water residing at local hydrophilic sites, such as alcohol groups, in polymers. Utilization of the HSP affinity between molecules or segments of molecules is a viable way to control self-assembly. See also Chapter 18.

SWELLING — EXAMPLES

The correlation for swelling of polypropylene reported in Table 5.3 is based on solvent uptake data reported by Lieberman and Barbe at 22°C.[19] The limit of 0.5% was arbitrarily set to differentiate good solvents from bad ones. As mentioned earlier, experience has shown that a different limit usually gives different parameters. It should be noted that swelling data reflect the properties of the regions in the polymer where the solvent has chosen to reside because of energetic similarity (self-assembly). The principle is not necessarily "like dissolves like," but rather "like seeks like." If the solvent is homogeneously distributed in the polymer, the solubility parameters found will reflect the properties of the whole polymer. Crystalline regions will not contain solvent. If the solvent collects locally in regions with chemical groups different from the bulk of the polymer, then the HSP so derived will reflect at least partially the physical nature of these chemical groups. The parameters reported in Table 5.3 seem appropriate for what is expected in terms of low polarity and low hydrogen-bonding properties for a polypropylene-type polymer.

An example of a characterization using swelling data that did not result in a good correlation is that for Viton® (The Du Pont Company, Wilmington, DE). This problem has been discussed by Zellers and Zhang[11,12] and is also discussed in Chapter 13. If one tries to force-fit data where there are several different comonomers into a single HSP sphere, the result is usually reflected in a poor correlation coefficient. Figure 13.3 shows that improvements can be made by using a separate sphere for each comonomer. One reason for the poor correlation of swelling behavior is that Viton is not a homopolymer, and also contains a cross-linking chemical. The different segments have different affinities. Indeed, there are several qualities of Viton, each of which has significantly differing chemical resistance. Swelling of Viton has also been treated by Evans and Hardy[20] in connection with predictions related to chemical protective clothing, and by Nielsen and Hansen,[21] who presented curves of swelling as a function of the RED number.

MELTING POINT DETERMINATIONS — EFFECT OF TEMPERATURE

Partly crystalline polymers that are placed in different liquids will have melting points which are lowered to a degree depending on the solvent quality of the individual liquids. The melting points of polyvinylidine chloride (PVDC) have been measured in different solvents.[22] These data have been analyzed by evaluating solubility parameter regions based on those solvents which dissolve the polymer at 110°C and above and also at 130°C and above. As expected, there are more solvents which dissolve the semicrystalline polymer at the higher temperature. The results for these correlations are included in Table 5.3. The main reasons for the somewhat lower data fit at 130°C include two nondissolving solvents within the solubility parameter sphere. These are dimethyl phthalate, where the large molecular size is a factor, and benzyl alcohol, where temperature effects can be larger than expected compared with the other solvents as discussed later and in Chapter 1. The solubility parameters for PVDC at this temperature, based on tabulated solvent values at 25°C, are not affected significantly by this type of situation. A single room temperature solvent for PVDC

is reported by Wessling.[22] This is hexamethylphosphoramide and its solubility parameters are also reported in Table 5.3 for comparison. The change in the values of the individual solubility parameters with temperature is discussed in Chapter 1 (Equation 1.16 to Equation 1.18). Chapter 3 also treats the temperature dependence of the HSP. See also Chapter 10 where the HSP of specifically carbon dioxide are treated in depth as a function of temperature and pressure.

ENVIRONMENTAL STRESS CRACKING

Environmental stress cracking (ESC) is unfortunately a very frequent mode of failure for plastics. For this reason a whole chapter is devoted to the topic (see Chapter 14). It has been possible to correlate HSP with ESC phenomena, and this can also provide an estimate of the HSP for the given polymers. Care is advised since the stress/strain level is important, as is the molecular size and shape of the chemicals involved. Several collections of ESC data in the older literature[23–25] should not be forgotten in these days of "Internet and only Internet." Such collections have particular value as it is considered impossible to get a commercially available polymer without some additives. These can also affect ESC behavior. These older data were the basis of the ESC correlations given in Chapter 14.

INTRINSIC VISCOSITY MEASUREMENTS

One of the more promising methods to evaluate polymer HSP for limited data is that using the intrinsic viscosity. Van Dyk et al. found a correlation with the intrinsic viscosity of an acrylic polymer (polyethyl methacrylate) in various solvents and the polymer HSP[26] (see the discussion on polymer compatibility in Chapter 8).

Segarceanu and Leca[27] have devised a method to calculate the polymer HSP from data on its intrinsic viscosity in different solvents. The intrinsic viscosities will be higher in the better solvents because of greater interaction and greater polymer chain extension. The intrinsic viscosity gives an indication of the solvent quality. It has been used earlier to calculate the Flory–Huggins chi parameter, for example.[28]

In the new technique, the intrinsic viscosities are normalized by the intrinsic viscosity of that solvent giving the highest value. These normalized data (numbers are 1.0 or less) are then used in a weighted averaging technique to arrive at the center of the Hansen sphere.

$$\delta_{D2} = \Sigma(\delta_{Di} \times [\eta]_i)/\Sigma[\eta]_i \tag{5.4}$$

$$\delta_{P2} = \Sigma(\delta_{Pi} \times [\eta]_i)/\Sigma[\eta]_i \tag{5.5}$$

$$\delta_{H2} = \Sigma(\delta_{Hi} \times [\eta]_i)/\Sigma[\eta]_i \tag{5.6}$$

The subscript 2 is for the polymer, and the respective solvents are indicated by an "i." The intrinsic viscosity in the i-th solvent is given by $[\eta]_i$.

Those solvents with the greatest weighting factor have higher intrinsic viscosities and are closest to the geometric center of the sphere. Those solvents which do not dissolve the polymer were assumed to have a zero weighting factor. The HSP for a polyesterimide were reported as an example. HSP values were assigned both by the "classical" evaluation and with this newer approach. These data are included as the first entries in Table 5.5. This is a very promising method of arriving at the polymer HSP with limited data.

There are several aspects of this work which deserve comment. It was demonstrated earlier that many polymers have higher solubility parameters than any of the solvents which are or can be used to test them. The present method only allows for polymer HSP within the range attainable

TABLE 5.5
HSP Data for the Same Polyesterimide
Polymer Based on Data Given in
Reference 27

Correlation	δ_D	δ_P	δ_D	Ro	FIT
Classical[a1]	17.4	12.3	8.6	4.1	—
New[a1]	18.0	11.1	8.8	8.6	—
HSP SPHERE[a]	20.0	11.0	10.0	8.3	1.000
HSP SPHERE[b]	19.0	11.0	9.0	7.0	1.000
Classical[a]					0.426
Classical[b]					0.447
New[a]					0.506
New[b]					0.364

Note: Units are MPa$^{1/2}$.

[a] Indicates use of the solubility parameters for the solvents given in Reference 27.
[b] Indicates use of the solvent HSP data in the author's files.

by the test solvents. The method will lead to values that are too low in some cases, including the example with the polyesterimide used as an example in Segarceanu and Leca.[27] It is not surprising that the polymer HSP are often higher than solvent HSP, as they are in a physical state between that of a liquid and a solid. When the cohesion energy becomes too high, a material is a solid rather than a liquid. Low molecular weight solids frequently have HSP somewhat higher than the HSP of liquids. Many examples can be given, including urea, ethylene carbonate, etc.

When the data (as soluble or not) for the 11 solvents were processed by the SPHERE computer program, the parameters found were those given by the third set of HSP in Table 5.5. The agreement with the "new" method is acceptable, even though none of the test solvents have δ_d as high as that of the polymer. Further inspection showed that the solubility parameters used in the study were not in agreement with those published in the latest reference to Hansen listed by Segarceanu and Leca.[27] It also appears that the radius of the HSP sphere for the classical determination is in error, being far too low.

To further clarify the situation, several runs with the SPHERE program were done with the parameters listed in this book, as well as with those listed in the article being discussed. In both cases the data fit is not good for the HSP reported by Segarceanu and Leca.[27] In the classical case, the data fit is only 0.426 (1.0 is perfect), and four of the five good solvents are located outside of the sphere. Only N-methyl-2-pyrrolidone is inside. In the new case, the data fit is not much better, being 0.506. Here, four of the five bad solvents are inside the sphere with only one being outside. It has been possible to estimate the polymer parameters within acceptable variation, but the radius of the sphere has not been accounted for in a satisfactory manner.

Further inspection of the data suggests that morpholine, the solvent with the highest [η] that was used to normalize the data, is not as good as might have been expected from the intrinsic viscosity data. This can be seen in Table 5.6. The reason for this is unknown, but experience has shown that amines often are seen to react with various materials in a manner which does not allow their inclusion in correlations of the type discussed here.

To conclude this section, it is noted that a similar weighting technique was used by Zellers et al.[13,14] where the weighted measurements were solvent uptake by elastomers customarily used to make chemical protective clothing. The same precautions must be taken in analyzing this type of

TABLE 5.6
Calculated Solubility SPHERE for Polyesterimide (Listed in RED Order)

D = 19.0 P = 11.0 H = 9.0 RAD = 7.0 FIT = 1.000 NO = 11

Solvent	$[\eta]_N^a$	D	P	H	SOLUB	RED	V
Methyl-2-pyrrolidone	0.970	18.0	12.3	7.2	1	0.427	96.5
Dimethyl formamide	0.947	17.4	13.7	11.3	1	0.682	77.0
Dimethyl sulfoxide	0.182	18.4	16.4	10.2	1	0.809	71.3
γ-Butyrolactone	0.689	19.0	16.6	7.4	1	0.832	76.8
Morpholine	1.000	18.8	4.9	9.2	1	0.874	87.1
Cyclohexanone	0.718	17.8	6.3	5.1	1	0.937	104.0
Diacetone alcohol	—	15.8	8.2	10.8	0	1.031	124.2
Acetone	—	15.5	10.4	7.0	0	1.044	74.0
Diethylene glycol monomethyl ether	—	16.2	7.8	12.6	0	1.055	118.0
Ethylene glycol monoethyl ether	—	16.2	9.2	14.3	0	1.131	97.8
Ethylene glycol monoethyl ether acetate	—	15.9	4.7	10.6	0	1.283	136.1

Note: Units are MPa$^{1/2}$.

[a] Normalized intrinsic viscosity data from Reference 27.

measurement, but as the polymers studied were reasonably nonpolar, some of the solvents had HSP which were higher than those of the polymers studied. Zellers et al.[14] and Athey[29] also describe multiple variable statistical analysis techniques to find the HSP of a given polymer. Barton's work[6] contains many literature sources of intrinsic viscosity studies using the solubility parameter for interpretation.

OTHER MEASUREMENT TECHNIQUES

There are many other techniques to differentiate between the behavior of different solvents in contact with a polymer. Many of these are discussed in the following chapters and will not be treated here. These include permeation measurements, chemical resistance determinations of various kinds including ESC, and surface attack, etc. Some of the techniques can be very useful, depending on the polymer involved. Others will present problems because of the probable influence of other factors such as solvent molar volume and length of time before attainment of equilibrium. Several of these phenomena can be correlated with HSP, but the techniques used in the measurements will present problems in using the data for direct HSP characterization of polymers because other effects are also important.

CONCLUSION

HSP for polymers can be evaluated experimentally by correlations of data where a suitably large number of well-chosen solvents are brought into contact with the polymer. The observed behavior which can be correlated includes true solubility, swelling, weight gain, dimensional change, degree of surface attack, reduction of melting point, permeation rate, breakthrough time, and tensile strength reduction. Correlations for simple evaluations of chemical resistance of the suitable-or-not type and ESC are also possible.

In each case, the molecular size of the liquids used can affect the result and should be considered in some way. The use of water as a test liquid is not recommended for these purposes.

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