

## **Application and Prediction of Solubility Parameters for Polymer/Solvent Systems.**

A quantitative measure of the cohesive properties of a substance is the *cohesive energy*. The cohesive energy per unit of volume is called *cohesive energy density*. The latter is closely related to the *internal pressure*, a quantity appearing in the equation of state.

The square root of cohesive energy density is called *solubility parameter*. It is widely used for correlating polymer solvent interactions. As a refinement, three solubility parameter components can be distinguished, representing dispersion, polar, and hydrogen bond interactions.

Although rigorous additivity rules are not applicable in this case, a fair estimation of the cohesive energy and the solubility parameter of polymers can be made by group contribution methods.

### ***INTRODUCTION***

The cohesive properties of a polymer find direct expression in its solubility in organic liquids. The cohesive properties of a substance are expressed quantitatively in the cohesive energy. This quantity is closely related to the internal pressure, a parameter appearing in the equation of state of the substance.

As early as 1916 Hildebrand pointed out that the order of solubility of a given solute in a series of solvents is determined by the internal pressures of the solvents. Later Scatchard(1931) introduced the concept of "cohesive energy density" into Hildebrand's theories, identifying this quantity with the cohesive energy per unit volume. Finally Hildebrand(1936) gave a comprehensive treatment of this concept and proposed the square root of the cohesive energy density as a parameter identifying the behavior of specific solvents. In 1949 he proposed the term solubility parameter and symbol  $\delta$ .

The solubility of a given polymer in various solvents is largely determined by its chemical structure. As a general rule, structural similarity favours solubility. In terms of the above-mentioned quantities this means that the solubility of a given polymer

and in a given solvent is favored if the solubility parameters of polymer is always defined as the squared root of the cohesive energy density in amorphous state at room temperature. The greater part of this chapter will be devoted to the cohesive energy and the solubility parameter, and to the correlation of these quantities with chemical structure.

Besides the chemical structure, also the physical state of a polymer is important for its solubility properties. Crystalline polymers are relatively insoluble and often dissolve only at temperature slightly below their crystalline melting points.

As a general rule, the solubility decreases as the molecular mass of the solute increases. This property can be used to fractionate polymers according to molecular mass.

Several applications of polymer/solvents systems are summarized as follow:

**Coatings.** Solvents in paints and varnishes dissolve resins that provide protective coating and support pigment and resin on the surface. Formulation of the solvent system is important because it controls ease and method of application (spraying vs brushing, for example), drying time, and nature of the resin film. New regulations from the EPA and DSHA reflecting both environment and safety requirements have caused many reformulations. This also has resulted in a shift toward water-base rather than solvent-base systems for some applications (see Coatings, industrial; Paint). However, some states have exempted the use of 1,1,1-trichloroethane and methylene chloride.

**Printing Inks.** The preparation of a printing ink is similar to a paint in that a resin and pigment must be blended with a solvent to produce a coating. For solvents used in printing inks, the solvents must evaporate very fast. However, because of the resins used, the solvents are usually petroleum products (see Inks)

**Staining and Wood Treatment.** Treating is required when wood is to be used in exterior applications to provide protection from weathering and to prevent attack from insects and fungi which cause decay. The solvents contain insecticides and fungicides which pass into the wood. Pigmentation and resin can be added to the solvent to produce wood stains as well as protective coatings (see Inks)

## A. COHESIVE ENERGY

### *Definitions*

The cohesive energy  $E_{\text{coh}}$  of a substance in a condensed state is defined as the increase in internal energy  $U$  per mole of substance if all the intermolecular forces are eliminated:

the cohesive energy  $\equiv E_{\text{coh}} = \Delta U$  (dimension: J/mol)

Directly related to the cohesive energy are the quantities

cohesive energy density:  $e_{\text{coh}} \equiv \frac{E_{\text{coh}}}{V}$  (at 298K) (dimension: J/cm<sup>3</sup>)

solubility parameter  $\delta = \left( \frac{E_{\text{coh}}}{V} \right)^{\frac{1}{2}} \equiv e_{\text{coh}}^{\frac{1}{2}}$  (at 298K) (dimension: J<sup>1/2</sup>/cm<sup>3/2</sup>)

## B. SOLUBILITY

### *The solubility parameter*

At first sight it is rather unpractical to use a quantity  $\delta$  with dimensions J<sup>1/2</sup>/cm<sup>3/2</sup> instead of the cohesive energy. The definition of  $\delta$  is based, however, on thermodynamic considerations, as will be discussed below. In the course of time the values of  $\delta$ , expressed in cal<sup>1/2</sup>/cm<sup>3/2</sup>, have become familiar quantities for many investigators. In this connection the change to SI units has some disadvantages. Conversion of cal<sup>1/2</sup>/cm<sup>3/2</sup> into J<sup>1/2</sup>/cm<sup>3/2</sup> is simple, however, as it only requires multiplication by a factor of 2 (2.046 to be exact).

The thermodynamic criteria of solubility are based on the free energy of mixing  $\Delta G_M$ . Two substances are mutually soluble if  $\Delta G_M$  is negative. By definition,

$$\Delta G_M = \Delta H_M - T \Delta S_M \quad (1)$$

where

$\Delta H_M$  = enthalpy of mixing

$\Delta S_M$  = entropy of mixing.

As  $\Delta S_M$  is generally positive, there is a certain limitation positive value of  $\Delta H_M$  below which dissolution is possible.

As early as 1916 Hildebrand tried to correlate solubility with the cohesive properties of the solvents. In 1949 he proposed the term solubility parameter and the symbol  $\delta$ , as defined in the beginning of this chapter.

According to Hildebrand, the enthalpy of mixing can be calculated by

$$\Delta h_M = \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \quad (2)$$

where

$\Delta h_M$  = enthalpy of mixing per unit volume

$\phi_1$  and  $\phi_2$  = volume fraction of components 1 and 2

$\delta_1$  and  $\delta_2$  = solubility parameters of components 1 and 2.

Eq. (2) predicts that  $\Delta G_M = 0$  if  $\delta_1 = \delta_2$ , so that two substances with equal solubility parameters should be mutually soluble due to the negative entropy factor. This in accordance with general rule that chemical and structure similarity favours solubility. As the difference between  $\delta_1$  and  $\delta_2$  increases, the tendency towards dissolution decreases.

We may conclude that as a requirement for the solubility of a polymer P in a solvent S, the quantity  $(\delta_P - \delta_S)^2$  has to be small, as small as possible.

The solubility parameters of a given material can be calculated either from the cohesive energy, or from the molar attraction constant  $F$ , as  $\delta = F/V$ .

In the derivation of eq. (2) it was assumed that no specific forces are active between the structural units of the substances involved. Therefore it does not hold for crystalline polymers.

Also if one of the substances involved contains strongly polar groups or hydrogen bridges,  $\Delta H_M$  may become higher than predicted by eq. (2), so that  $\Delta H_M$  becomes positive even for  $\delta_1 = \delta_2$  and dissolution does not occur. Conversely, if both substances contain polar groups or hydrogen bridges, solubility may be promoted.

For these reasons a more refined treatment of the solubility parameter concept is often necessary, especially for interactions between polymers and solvents. Nevertheless, the solubility parameters of polymers and solvents are important quantities in all phenomena involving interactions between polymers and solvents.

Evidently, the most important application of the solubility parameters to be discussed in this paper is the prediction of the solubility of polymers in various solvents. A first requirement of mutual solubility is that the solubility parameter of the polymer  $\delta_F$  and that of the solvent  $\delta_S$  do not differ too much.

This requirement, however, is not sufficient. There are combinations of polymer and solvent for which  $\delta_P \approx \delta_S$ , but yet do not show mutual solubility. Mutual solubility only occurs if the degree of hydrogen bonding is about equal. This led Burrell(1955) towards a division of solvents into three classes, viz. poorly, moderately and strongly hydrogen bonded. In combination with the total solubility parameter  $\delta$  a considerably improved classification of solvents is obtained.

### ***Refinements of the solubility parameter concept***

In the derivation of eq.(2) by Hildebrand only dispersion forces between structural units have been taken into account. For many liquids and amorphous polymers, however, the cohesive energy is also dependent on the interaction between polar groups and on hydrogen bonding. In these cases the solubility parameter as defined corresponds with the total cohesive energy.

Formally, the cohesive energy may be divided into three parts, corresponding with

the three types of interaction forces

$$\mathbf{E}_{\text{coh}} = \mathbf{E}_d + \mathbf{E}_p + \mathbf{E}_h \quad (3)$$

where

$\mathbf{E}_d$  = contribution of dispersion forces

$\mathbf{E}_p$  = contribution of polar forces

$\mathbf{E}_h$  = contribution of hydrogen bonding

The corresponding equation for the solubility parameter is

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (4)$$

The equivalent of eq.(4) becomes

$$\Delta h_M = \phi_1 \phi_2 [ (\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2 ] \quad (5)$$

Unfortunately, values of  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$  cannot be determined directly.

There are, in principle, two ways for a more intricate use the solubility parameter concept:

- a. the use of other measurable physical quantities besides the solubility parameter for expressing the solvent properties of a liquid;
- b. indirect determination of the solubility parameter components  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$ .

The first method was used by Beerbower et al.(1967), who expressed the amount of hydrogen bonding energy by the *hydrogen bonding number*  $\Delta\nu$ . This quantity was defined by Gordy and Stanford(1939)-1941) as the shift of the infrared absorption band in the 4  $\mu\text{m}$  range occurring when a given liquid is added to a solution of deuterated methanol in benzene.

Beerbower et al. plotted the data for various solvents in a diagram with the

solubility parameter  $\delta$  along the horizontal axis and the hydrogen bonding number  $\Delta v$  along the vertical axis. All the solvents in which a given polymer is soluble fall within a certain region. As an example, fig. 1 shows such a diameter for polystyrene.

Crowley et al.(1966,1967) used an extension of this method by including the dipole moment of the solvent in the characterization. However, as this involves a comparison of a number of solvents in a three-dimensional system, the method is impractical.

The second method was developed by Hansen(1967,1969). Hansen presumed the applicability of eqn.(4) and (5) and developed a method for the determination of  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$  for a number of solvents. The value of  $\Delta \delta_a$  of a given solvent was assumed to be equal to that of a non-polar substance(e. g. hydrocarbon) of about the same chemical structure. This permitted the calculation of  $\delta_p^2 + \delta_h^2 = \delta^2 - \delta_d^2 (= \delta_a^2)$ .

Now Hansen determined experimentally the solubility of a number of polymers in a series of solvents. All the solvents were characterized by a point in a three-dimensional structure, in which  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$  could be plotted on three mutually perpendicular axis. The values of  $\delta_p$ ,  $\delta_h$  for the various solvents were shifted until all the solvents in which a given polymer was soluble were close together in space.

For comparison also values of the dipole moment  $\mu$  and the hydrogen bonding number  $\Delta v$  are mentioned.

Hansen also determined  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$  of the polymers involved, being the coordinates of the center of the solvents region in his three dimensional structure.

The method of Hansen has the disadvantage that three-dimensional structures are necessary for a graphical representation of the interaction between polymers and solvents. For practical applications a two-dimensional method is to be preferred.

Thermodynamic considerations led Bagley et al.(1971) to the conclusion that the effects of  $\delta_d$  and  $\delta_p$  show close similarity, while the effect of  $\delta_h$  is of a quite different nature. Accordingly, they introduced the parameter  $\delta_v = \sqrt{(\delta_d^2 + \delta_p^2)}$ . This

leads to a diagram in which  $\delta_v$  and  $\delta_h$  are plotted on the axes.

Such a diagram is shown in fig. 2 for the interaction between polystyrene and a number of solvents. The majority of the points for good solvents indeed fall in a single region of fig. 2. This region can approximately be delimited by a circle the centre of which is indicated by the symbol. Obviously, fig.2 is superior to fig. 1 in demarcating a solubility region.

A method of representation very similar to that of fig. 2 was proposed by Chen(1971). He introduced a quantity

$$\chi_{11} = \frac{V_S}{RT} [ (\delta_{dS} - \delta_{dP})^2 + (\delta_{hS} - \delta_{hP})^2 ] \quad (6)$$

where the subscripts S and P denote solvent and Polymer, respectively. The solubility data are then plotted in a  $\delta_h - \chi_H$ -diagram. A disadvantage of this method is that the characteristics of the polymer should be estimated beforehand.

Other two-dimensional methods for the representation of solubility data are the  $\delta_p - \delta_h$ -diagram proposed by Henry (1974), the  $\delta - \delta_h$ -diagram proposed by Hoernschemeyer(1974) or the  $\delta - \delta_a$ -diagram.

At the moment the  $\delta_v - \delta_h$ -diagram seems to be the most efficient way to represent polymer-solvent interaction.

### ***Solubility of polymers in solvents***

In the  $\delta_h - \delta_v$ -diagram the degree of solubility (volume of polymer per volume of solvent) can be indicated by a number. This is shown in fig.3 for the data of Kambour et al.(1973) on the solubility of polystyrene in a number of solvents.

The solubility region can approximately be delimited by a circle with a radius of about 5  $\delta$ -units. The center of this circle is indicated by the symbol\*; it has the coordinate values:  $\delta_v = 18$ ;  $\delta_h = 5$ . It can be seen that the solubility increases



approximately as the distance from the centre decreases.

As a general rule, polystyrene is soluble in solvents for which

$$|\sqrt{\delta_v - 18^2 + \delta_h - 5^2}| < 5 \quad (7)$$

The literature mentions analogous data for a number of other polymers, which will not be discussed here. When plotted in a  $\delta_h - \delta_v$ -diagram, they generally show the same type of picture. The reader should be warned, however, of the limited accuracy of this method. The diagrams give only an indication of solubility relationships and always show a number of deviating points.

### ***Solubility limits and Flory-temperature***

The solubility limits of a given polymer are closely related to the Flory-temperatures of the polymer in various solvents.

The Flory-temperature ( $\Theta_F$ ) is defined as the temperature where the partial molar free energy due to polymer-solvent interactions is zero, so that the polymer-solvent systems show ideal solution behavior. If  $T = \Theta_F$  the molecules can interpenetrate one another freely with no net interactions. At  $T < \Theta_F$  the molecules attract one another. If the temperature is much below  $\Theta_F$ , precipitation occurs.

Thermodynamical considerations have led to the following equation for the temperature at which phase separation of polymer solutions begins:

$$T_{cr} \approx \frac{\Theta_F}{1 + \frac{C}{M^2}} \quad \text{where } c \text{ is a constant for the polymer-solvent system.} \quad (8)$$

It is clear that the *Flory-temperature is the critical miscibility temperature in the limit of infinite molecular weight.*

Fox(1962) succeeded in correlating  $\Theta_F$ -temperatures of polymer-solvent systems

with the solubility parameter  $\delta_s$  of the solvent. plot of  $\delta_s$  as a function of  $\Theta_F$  are shown in fig.4.

At a given temperature, a solvent for the polymer should have a  $\delta$ -value approximately between the limits, indicated by the two straight lines in the figure.

An even better correlation of Flory-temperatures with solubility parameters can be given in a  $\delta_h - \delta_v$  diagram. This is shown in fig.5 for polystyrene. the circle drawn in fig.5 corresponds again with eq.(7).

### ***Prediction of solubility-parameter components***

The solubility parameter components  $\delta_d$ ,  $\delta_p$  and  $\delta_h$  (and their combinations  $\delta_a = \sqrt{\delta_p^2 + \delta_h^2}$  and  $\delta_v = \sqrt{\delta_d^2 + \delta_p^2}$ ) are known for a limited number of solvents only.

Therefore a method for predicting these quantities is valuable.

It is to be expected that the polar component  $\delta_p$  is correlated with the dipole moment  $\mu$  and that the hydrogen bonding component  $\delta_h$  is correlated with the hydrogen bonding number  $\Delta v$ . This is not of much use, however, as also  $\mu$  and  $\Delta v$  are only known for a limited number of solvents. A useful prediction method must be on the molecular structure of the solvent.

The available experimental data prove, however, that it is impossible to derive a simple system for an accurate prediction of solubility parameter components from the chemical structure. Especially the interaction of different structural groups in producing overall polar and hydrogen-bonding properties is so complicated that it does not obey simple rules.

If nevertheless such a prediction method is presented here, it does not pretend to give more than rather rough estimates. yet this may sometimes be preferable to a complete lack of data. Two approaches have been published, viz. that of Hoftyzer and Van krevelen (1976) and that of Holy (1985); in both methods the same basic assumption is made, that of Hasen:

$$E_{coh} = E_d + E_p + E_h \text{ (see eq.3), so:}$$

$$\delta_1^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \text{ (see eq. 4)}$$

1) *Method of Hoftyzer and Van Krevelen (1976)*

the solubility parameter components may be predicted from group contributions, using the following equations:

$$\delta_d = \frac{\sum F_{di}}{V} \quad (9)$$

$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V} \quad (10)$$

$$\delta_h = \sqrt{\frac{\sum E_{hi}}{V}} \quad (11)$$

This means that for the prediction of  $\delta_d$  the same type of formula is used as Small proposed for the prediction of the total solubility parameter  $\delta$ . The group contributions  $F_{di}$  to the dispersion component  $F_d$  of the molar attraction constant can simply be added.

The same method holds for  $\delta_p$ , as long as only one polar group is present. To correct for the interaction of polar groups, the form of equation (10) has been chosen.

The polar component is still further reduced, if two identical polar groups are present in a symmetrical position. To take this effect into account, the value of  $\delta_p$ , calculated with eq.(11) must be multiplied by a symmetry factor of:

0.5 for one plane of symmetry

0.25 for two planes of symmetry

0 for more planes of symmetry

The F-method is not applicable to the calculation of  $\delta_h$ . It has already been stated by Hansen that the hydrogen bonding energy  $E_{hi}$  per structural group is approximately constant. This leads to the form of equation (11). For molecules with several planes of symmetry,  $\delta_h = 0$ .

*Example 1.*

Estimate the solubility parameter component of diacetone alcohol

*Solution*

The molar volume  $V=123.8\text{cm}^3/\text{mol}$ . Addition of the group contribution gives

	$F_{di}$	$F_{Pi}^2$	$E_{hi}$
3 -CH <sub>3</sub>	1260	0	0
-CH <sub>2</sub> -	270	0	0
>C<	-70	0	0
-CO-	290	593000	2000
-OH	210	250000	20000
	1960	843000	22000

According to equation (9) to (10)

$$\delta_d = \frac{\sum F_{di}}{V} = \frac{1960}{123.8} = 15.8 \text{ J}^{1/2} / \text{cm}^3$$

$$\delta_p = \frac{\sqrt{\sum F_{Pi}^2}}{V} = \frac{\sqrt{843000}}{123.8} = 7.4 \text{ J}^{1/2} / \text{cm}^3$$

$$\delta_h = \sqrt{\frac{\sum E_{hi}}{V}} = \sqrt{\frac{22000}{123.8}} = 13.3 \text{ J}^{1/2} / \text{cm}^3$$

The literature values are  $\delta_d=15.7$

$$\delta_p=8.2$$

$$\delta_h=10.9$$

From the calculated components an overall value of the solubility parameter is found:

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} = 21.9 \text{ J}^{1/2} / \text{cm}^3$$

The experimental values for  $\delta$  vary from 18.8 to 20.8  $J^{1/2} / cm^3$ .

## 2) Method of Hoy (1985, 1989)

Hoy's method is in many respects different from that of Hoftyzer and Van Krevelen. Table 7.9 gives a survey of the system of equations to be used. It contains four additive molar functions, a number of auxiliary equations and the final expressions for  $\delta_{t(\text{total})}$  and for the components of  $\delta$ .

$F_t$  is the molar attraction function,  $F_p$  its polar component (both as discussed earlier);  $V$  is the molar volume of the solvent molecule or the structural unit of the polymer.  $\Delta_T$  is the Lyderson correction for non-ideality, used in the auxiliary equations. The values for low-molecular liquids were derived by Lyderson (1955); the corresponding values for polymers, which are slightly different, have been derived by Hoy ( $\Delta_T^{(p)}$ ).

Of the other quantities in the auxiliary equations, the significance is the following:  $\alpha$  is the *molecular aggregation number*, describing the association of the molecules;  $\bar{n}$  is the number of repeating units per effective chain segment of the polymer.

It must be emphasized Hoy is the only author who uses a "base value" in the calculation of  $F_t$ , whereas he neglects a base value in  $V$ ; it was mentioned earlier that Traube (1895) already proved that for the additive calculation of the molar volume of liquids a base value has to be used.

Hoy's method will now be illustrated by two numerical examples.

### Example 2.

Estimate the value of  $\delta$  and the  $\delta$ -components of polyvinyl acetate

#### Solution

Groups	$F_1$	$F_p$	$\Delta_T^{(p)}$	$V$
-CH <sub>4</sub>	303.5	0	0.022	21.55
-CH <sub>2</sub> -	269.0	0	0.020	15.55
-CH<	176.0	0	0.013	9.56
-COO-	640	528	0.050	23.7
sum	1388.5	528	0.105	70.36

Base value=277

$$\alpha = \frac{777 \times 0.105}{70.4} = 1.16; \bar{n} = \frac{0.5}{0.105} = 4.76$$

$$\text{So } \delta_t = \frac{1388.5}{70.4} + \frac{277/4.76}{70.4} = 19.72 + 0.83 = 20.55$$

$$\delta_p = 20.55 \left( \frac{1}{1.16} \cdot \frac{528}{1447} \right)^{\frac{1}{2}} = 20.55 \times 0.56 = 11.5$$

$$\delta_h = 20.55 \left( \frac{0.16}{1.16} \right)^{\frac{1}{2}} = 20.55 \times 0.37 = 7.6$$

$$\delta_d = (20.55^2 - 11.5^2 - 7.6^2)^{\frac{1}{2}} = 15.2$$

The comparison with other values is as follows:

	exp.	Small	Hansen	Hoflyzer -Van Krevelen	Hoy
$\delta_t$	19.1-22.6	19.2	23.1	19.4	20.55
$\delta_d$	-	-	19.0	16.0	15.2
$\delta_p$	-	-	10.2	6.8	11.5
$\delta_h$	-	-	8.2	8.5	7.6

The results of the two algorithmic methods for estimation of the solubility parameter and its components (Hoflyzer-Van Krevelen and Hoy) are of the same order in accuracy (10%), So the safest way for estimation is to apply both methods, taking the average results.

To conclude we give the full equation which determines the solubility of a polymer in an organic liquid:

$$\overline{\Delta\delta} = [ (\delta_{d,p} - \delta_{d,s})^2 + (\delta_{p,p} - \delta_{p,s})^2 + (\delta_{h,p} - \delta_{h,s})^2 ]^{\frac{1}{2}} \quad (12)$$

For a good solubility  $\overline{\Delta\delta}$  must be small ( $\geq 5$ )

### ***Influence of crystallinity***

It was pointed out from the beginning that the concept of the solubility parameter was applicable only to amorphous polymers.

In order to adapt the method to highly crystalline polymers some way must be

found to deal with the heat of fusion ( $\Delta H_m$ ) in the free enthalpy equation:

$$\Delta G_m = \{\Delta H_M + \Delta H_m\} - T\{\Delta S_M + \Delta S_m\}$$

Highly crystalline polymers such as polyethylene and poly(tetrafluoroethylene) are insoluble in all solvents at room temperature. These polymers, however, obey the solubility parameters rules at

$$T \geq 0.9T_m$$

For instance, polyethylene becomes soluble above 80°C. Furthermore, crystalline polymer do obey the rules even at room temperature in so far as swelling behavior is concerned. This again is a demonstration that crystalline regions serve as apparent(physical) cross-links.

some crystalline polymers with strong hydrogen bonding groups can be made to dissolve at room temperature. But in these cases a very specific interaction between polymer and solvent must occur. For example, cellulose is soluble in 70% sulphuric acid and in aqueous ammonium thiocyanate; nylon 6,6 is soluble in phenol and in a 15% calcium chloride solution in methanol.

### ***Other applications of solubility parameter diagrams***

Solubility parameter diagrams, e.g.  $\delta_h$  - $\delta_v$ -diagrams, may be useful for the correlation of some phenomena attended with polymer-solvent interaction. these phenomena will only be mentioned here.

a. Characteristic parameters of dilute polymer solutions, e.g.:

- (1) the Mark-Houwink exponent  $\alpha$
- (2) the composition of solvent mixtures forming  $\Theta$ -solutions with a given polymer
- (3) partial density of polymers in solution

b. Deterioration of polymers by solvents, e.g.:

- (1) swelling of polymers by solvents
- (2) solvent crazing and cracking
- (3) decrease of mechanical properties, e.g. tensile strength

c. shrinkage of polymer fibres, immersed in solvents

d. Crystallization of polymers induced by solvents

All these applications may lead to better and more consistent values of the parameter components.

***Solubility of (semi-) rigid polymers***

During the last decades the interest in semi-rigid aromatic polymers (aramids and arylates a.o.) is increasing. Dissolving of these polymers may be very difficult and requires rather unusual solvent.



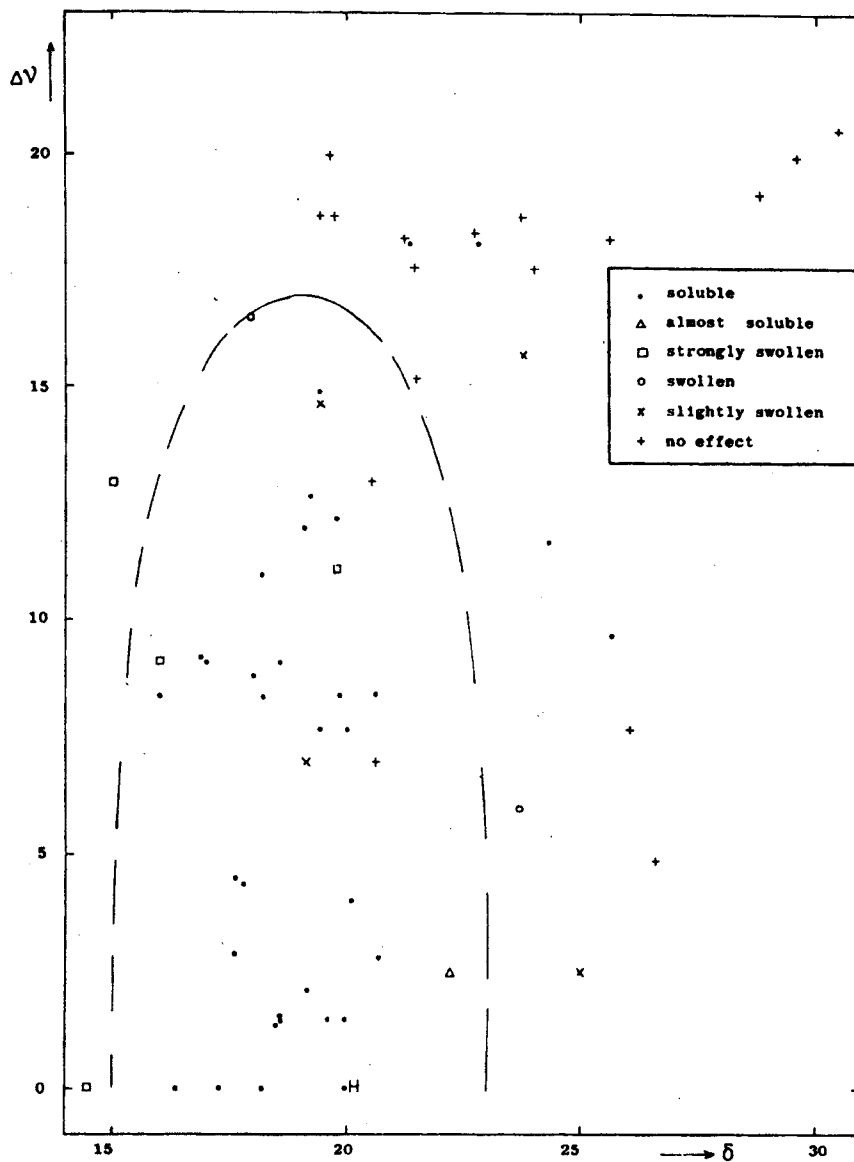


Fig. 1. Solubility of polystyrene in various solvents in the  $\Delta v - \delta$  diagram.

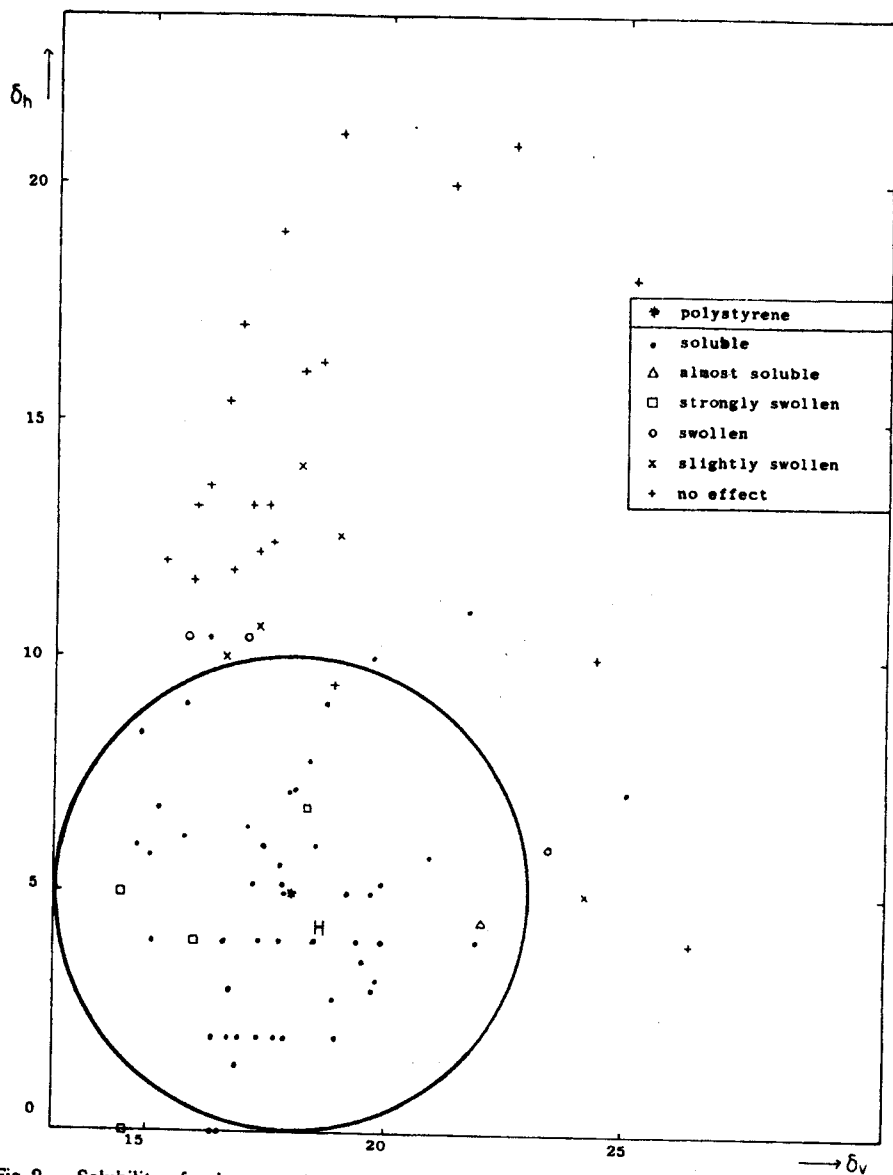
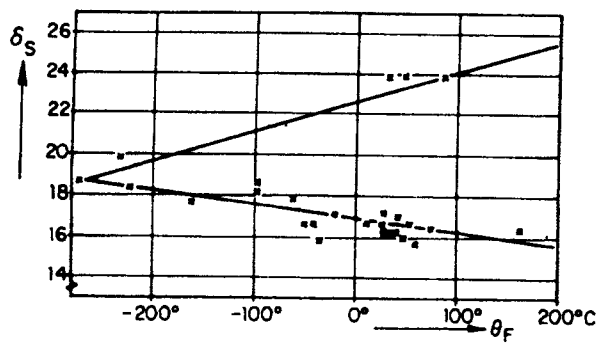
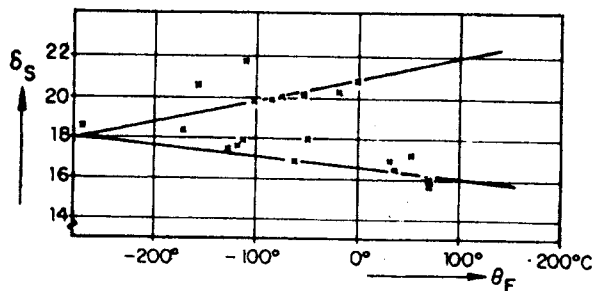


Fig. 2. Solubility of polystyrene in various solvents in the  $\delta_v - \delta_h$  diagram.

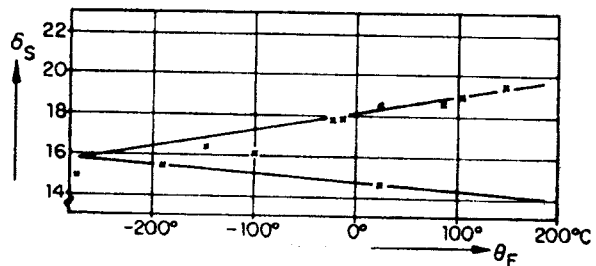




a) poly (methyl methacrylate).



b) polystyrene



c) polyisobutylene

Fig. 4. Solubility parameters and  $\theta$ -temperatures (Van Krevelen and Hoflyzer, 1967).

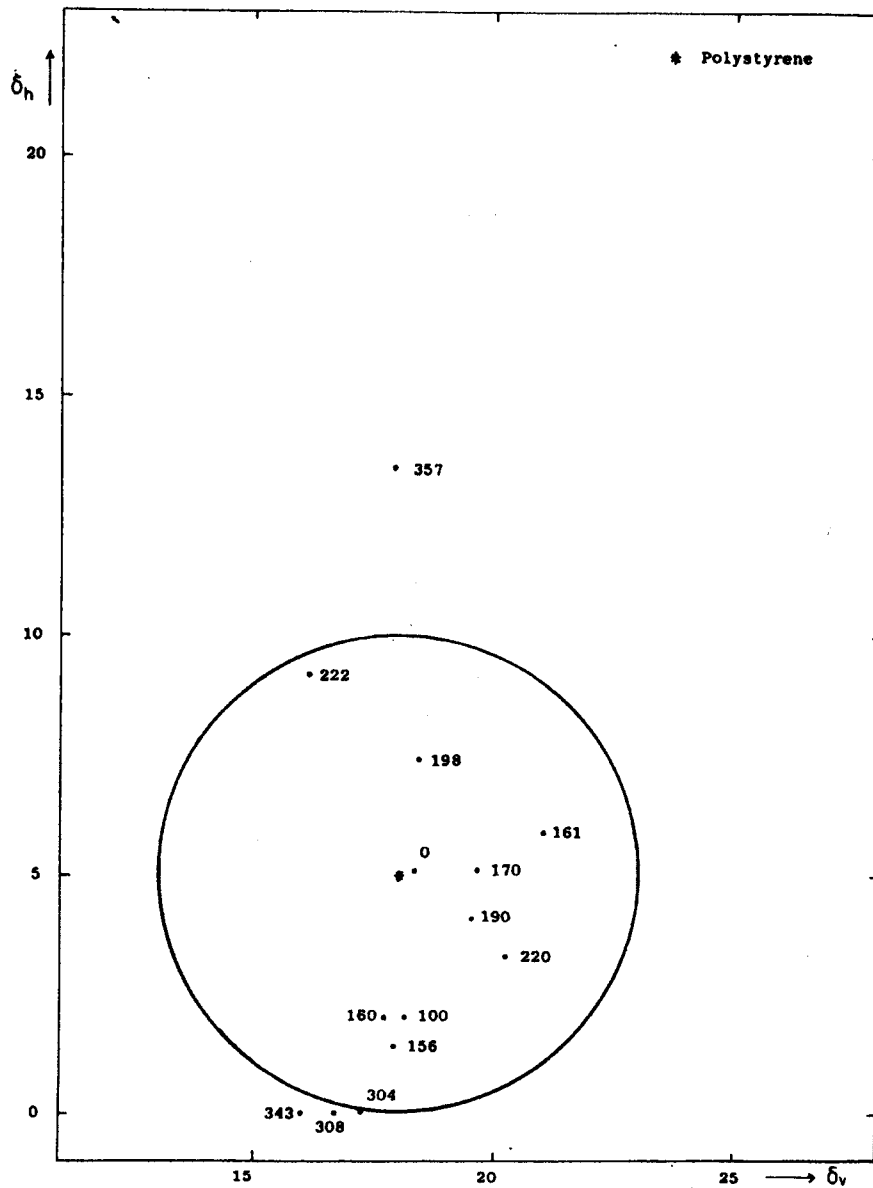


Fig. 5. Flory-temperatures of polystyrene in various solvents.

