

Solubility parameters of poly(4-acetoxystyrene) and poly(4-hydroxystyrene)

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The solubility parameters δ_2 of poly(4-acetoxystyrene) (PAS) and poly(4-hydroxystyrene) (PHS) were determined by the viscosity measurements and the turbidimetric measurements proposed by Mangaraj *et al.*¹ and Suh and Clarke², respectively. The δ_2 values were compared with those estimated by the calculation methods proposed by Small³, Hoy⁴ and Fedors⁵. The δ_2 values of PAS and PHS were also determined by the method of Hansen⁶ in order to obtain additional information on the components of the intermolecular interaction between segments of these polymers. It was found that the δ_2 values of PAS and PHS are both considerably larger than those of other linear polymers, but the components of δ_2 concerning the dispersion force are almost the same among polystyrene derivatives including PAS and PHS. It was also found that the polar component of δ_2 values of PAS and PHS are nearly the same as those of poly(vinylacetate) and poly(methylmethacrylate). Finally, the components of δ_2 arising from the hydrogen-bonding formation of PHS are quite large compared with those of other polymers and these may be considered to be the origin of the characteristic properties of this polymer in solid and solution.

(Keywords: poly(4-acetoxystyrene); PAS; poly(4-hydroxystyrene); PHS; solubility parameter; thermodynamic interaction parameter; viscosity)

INTRODUCTION

In connection with the studies of poly(4-acetoxystyrene-co-4-hydroxystyrene) which can be obtained by partial hydrolysis of poly(4-acetoxystyrene) (PAS), we reported that PAS and poly(4-hydroxystyrene) (PHS), which can be obtained by complete hydrolysis of PAS, are widely different in their solubility properties^{7,8}. For example, PAS is soluble in benzene and insoluble in aliphatic alcohols, while PHS is soluble in aliphatic alcohols and insoluble in non-polar solvents such as aliphatic and aromatic hydrocarbons.

These solubility characteristics should be reflected in various thermodynamic interaction parameters such as the Flory-Huggins enthalpy and entropy parameters, κ_1 and ψ_1 . In fact, the values of κ_1 and ψ_1 were positive in all solvents measured for PAS. In contrast, they were all negative for PHS in all solvents measured^{7,8}. These differences are attributed to the intra- and intermolecular interactions, including hydrogen bond formation due to the presence of phenolic hydroxyl groups in PHS. It is meaningful, therefore, to confirm this presumption by estimating the solubility parameters of these two polymers.

The solubility parameter concept has found wide and increasing use in many areas of industrial and academic endeavour because of the simplicity with which significant predictions on solubility can be obtained. This concept is

generally applied to solvent selection in the industrial field, while the calculation of solubilities and thermodynamic properties have been the concerns mainly of theoretical workers.

The solubility parameter concept based on Hildebrand's theory of regular solution is simple and allows prediction of polymer properties⁹. The solubility parameter of a polymer can be related to the polymer-solvent interaction coefficient and also to the cohesive energy density of the polymer which gives information on the values of intermolecular forces in a polymer in the amorphous state. Therefore, solubility-parameter studies can provide systematic information on polymer-solvent interactions for any polymer, if the solubility test of the polymer is performed with various kinds of solvents.

The solubility parameters of polymers can be obtained by solution viscosity measurements¹. In this way a single solubility parameter δ that is based on the theory developed for mixing of nonpolar substances is obtained. However, many of the solvents in common use are polar and the concept of a solubility parameter has been extended to polar polymers.

We have adopted both the single and the three dimensional solubility parameter approach as developed by Hansen^{6,10-12}, in which the solubility parameter is divided into three contributions; dispersion δ_d , polar δ_p , and hydrogen bonding δ_h . The three dimensional solubility parameter approach gives the additional infor-

Table 1 Limiting viscosity numbers of PAS and PHS, and solubility parameters for each solvent

Solvent	δ_1^*	V_1	$[\eta]$	
			PAS	PHS
Propylene glycol	14.8	73.7	—	3.65
Methanol	14.3	40.7	—	3.79
Dimethyl sulphoxide	12.9	71.3	0.495	4.89
Dimethylformamide	12.1	77.4	0.580	5.26
Aniline	11.0	91.5	0.656	—
2-Butanol	10.9	92.4	—	5.11
Dioxane	9.87	85.7	0.558	4.08
Tetrahydrofuran	9.52	98.2	0.466	3.28
Ethyl acetate	9.10	98.5	0.425	2.57
4-Methyl-2-pentanone	8.57	125	0.225	—

*Values of δ_1 for solvents were cited from the literature^{6,10,16}

mation on the effect of structural modifications on the polymer chain in the solubility behaviour^{13,14}.

The method described above seems to reliably predict the solubilities of a polar polymer in ordinary organic solvents. It will also enable us to determine the theta solvents for the polymer.

In this paper we report the solubility parameters of PAS and PHS determined by means of as many experimental and calculation methods as possible. The results are discussed in connection with the constitution of these polymers and other standard polymers including polystyrene.

EXPERIMENTAL

Materials

PAS and PHS used in this investigation were polymerized and fractionated according to a previously described method^{7,8}. All the solvents and other materials used were of reagent grade and purified according to the standard procedures except those used for preliminary solubility test.

Measurements

Viscosity measurements were carried out using Ubbelohde type viscometers in a water bath controlled at $25 \pm 0.01^\circ\text{C}$. Both shear rate and kinetic energy corrections were negligible. The limiting viscosity number $[\eta]$ was determined as a common intercept of η_{sp}/C versus C and $(\ln \eta_r)/C$ versus C , where η_r is the relative viscosity, η_{sp} is the specific viscosity, and C is the polymer concentration expressed in g/dl^{-1} .

Turbidimetric measurements proposed by Suh and Clarke² to determine solubility parameter of a polymer were carried out at $25 \pm 0.01^\circ\text{C}$ on solutions with concentrations of 0.2 g/dl^{-1} in several solvents. A non-solvent was slowly added to the solution to reach the cloud point at which the image of a copper wire situated behind the cell of each polymer solution became blurred by the solution turbidity. Two non-solvents, having higher and lower solubility parameters, respectively, were used for the turbidimetric titrations.

Densities of PAS and PHS were determined by means of a small pycnometer in a water bath controlled within $\pm 0.01^\circ\text{C}$ at 25°C .

RESULTS

It has been shown that, in general, the limiting viscosity numbers $[\eta]$ of a particular polymer sample are found to

reach a maximum, $[\eta]_{\text{max}}$, in the solvent which has the same solubility parameter as that of the polymer. In Table 1 the solubility parameter, δ_1 , and the molar volume, V_1 , of solvents used, and the limiting viscosity numbers for PAS and PHS samples measured in these solvents are presented. The plots of $[\eta]$ against δ_1 are shown in Figures 1 and 2. In fact, dull maxima are found in these figures around $11 (\text{cal cm}^{-3})^{1/2}$ and $12 (\text{cal cm}^{-3})^{1/2}$ for PAS and PHS, respectively. However, the maxima are not so sharp and hence the solubility parameters of the polymer, δ_2 , estimated from the maxima have large unavoidable uncertainty. We examined therefore the method of Mangaraj *et al.*¹ They assume that the limiting viscosity numbers can be represented by the following Gaussian function:

$$[\eta] = [\eta]_{\text{max}} \exp\{-V_1(\delta_1 - \delta_2)^2\} \quad (1)$$

The calculated values of $\{V_1^{-1}(\ln[\eta]_{\text{max}}/[\eta])\}^{1/2}$ are plotted against δ_1 in Figures 1 and 2 and approximate straight lines are drawn covering most points. The δ_2 values of PAS and PHS were established from the points of intersection of the lines with the abscissa, from which values of $11.1 (\text{cal cm}^{-3})^{1/2}$ for PAS and of $11.7 (\text{cal cm}^{-3})^{1/2}$ for PHS are obtained.

The second method used to determine the solubility parameters of polymers is the turbidimetric measurements proposed by Suh and Clarke². This method is based on the fact that the Flory-Huggins polymer-solvent interaction coefficient χ_1 can be divided into the

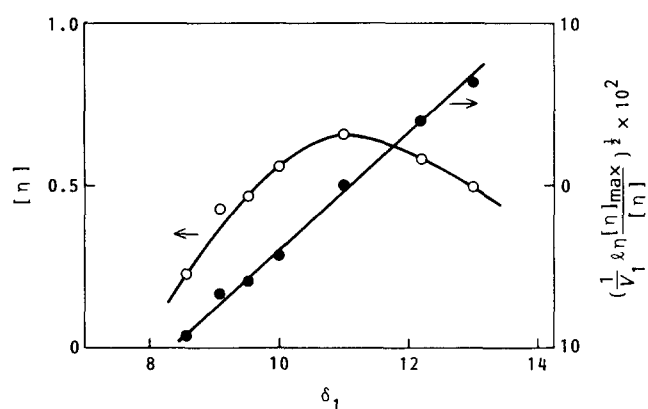


Figure 1 Determination of the solubility parameter δ_2 for PAS by viscosity measurements

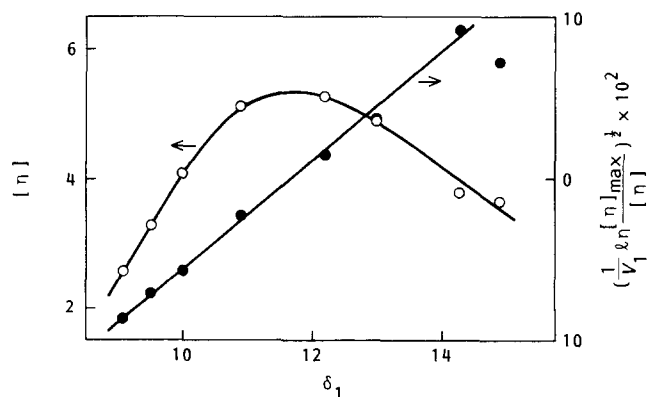


Figure 2 Determination of the solubility parameter δ_2 for PHS by viscosity measurements

Table 2 Results of turbidimetric measurements for PAS

Solvents	V_1 ($\text{cm}^3 \text{mol}^{-1}$)	ϕ_3		δ_1 ($\text{cal}^{1/2} \text{cm}^{-3/2}$)	δ_2' ($\text{cal}^{1/2} \text{cm}^{-3/2}$)
		hexane	methanol		
Acetic acid	57.5	0.29	0.38	10.5	10.6
Dioxane	85.7	0.33	0.65	10.0	10.6
Benzene	89.4	0.15	0.51	9.1	10.1
Tetrahydrofuran	98.2	0.25	0.54	9.5	10.3
Toluene	106.9	0.05	0.50	8.8	10.0
1,2-Dichlorobenzene	113.1	0.26	0.45	10.0	10.4

Table 3 Results of turbidimetric measurements for PHS

Solvents	V_1 ($\text{cm}^3 \text{mol}^{-1}$)	ϕ_3		δ_1 ($\text{cal}^{1/2} \text{cm}^{-3/2}$)	δ_2' ($\text{cal}^{1/2} \text{cm}^{-3/2}$)
		cyclo- hexane	DCB ^a		
Acetic acid	57.5	0.28	0.49	10.5	10.0
Dioxane	85.7	0.40	0.74	10.0	9.7
Tetrahydrofuran	98.2	0.35	0.83	9.5	9.5
Ethyl acetate	98.5	0.39	0.75	9.0	9.3
4-Methyl-2-pentanone	125.8	0.40	0.74	8.4	8.9
Butyl acetate	132.5	0.38	0.72	8.5	9.0

^a 1,2-dichlorobenzene

term of enthalpy χ_h and of entropy χ_s , i.e.:

$$\chi_1 = \chi_h + \chi_s \quad (2)$$

The quantities χ_h and χ_s correspond to κ_1 and $1/2 - \psi_1$ in the terminology of Flory¹⁵. The χ_h contribution is directly related to δ_2 , as follows:

$$\chi_h = (V_1/RT)(\delta_1 - \delta_2)^2 \quad (3)$$

This equation is necessarily used only for endothermic systems.

In this method, turbidimetric titrations are performed with two different non-solvents, one of a lower and one of a higher solubility parameter. Because the value of χ_h reaches a constant at the cloud point in dilute polymer solution, by equating the two expressions for each χ_h , the following relationship is obtained:

$$\frac{V_{m1}(\delta_2 - \delta_{m1})^2}{RT} = \frac{V_{mh}(\delta_2 - \delta_{mh})^2}{RT} \quad (4)$$

where V_{m1} and V_{mh} represent the molar volume of the mixtures of solvent and non-solvent of lower solubility parameter and those of higher solubility parameter at the cloud points respectively and, δ_{m1} and δ_{mh} represent corresponding solubility parameters of the mixed solvents.

Values of δ_m and V_m are calculated using the following approximations:

$$\delta_m = \phi_1\delta_1 + \phi_3\delta_3 \quad (5)$$

$$V_m = V_1V_3/(\phi_1V_3 + \phi_3V_1) \quad (6)$$

where the subscripts 1 and 3 refer to the solvent and non-solvent in the solution, ϕ and V are volume fractions and molar volume, respectively. Simplifying equation (4), the solubility parameter of a polymer can be obtained by the relation:

$$\delta_2 = (V_{m1}^{1/2}\delta_{m1} + V_{mh}^{1/2}\delta_{mh})/(V_{m1}^{1/2} + V_{mh}^{1/2}) \quad (7)$$

The experimental data obtained from turbidimetric titrations in different solvents of PAS with hexane and methanol as precipitants and of PHS with cyclohexane and 1,2-dichlorobenzene as precipitants are shown in

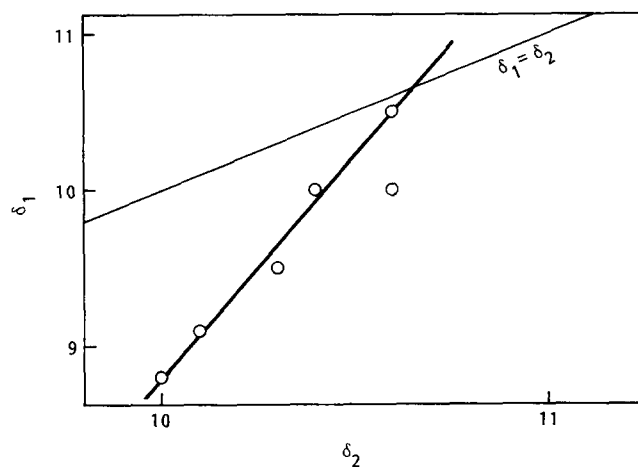
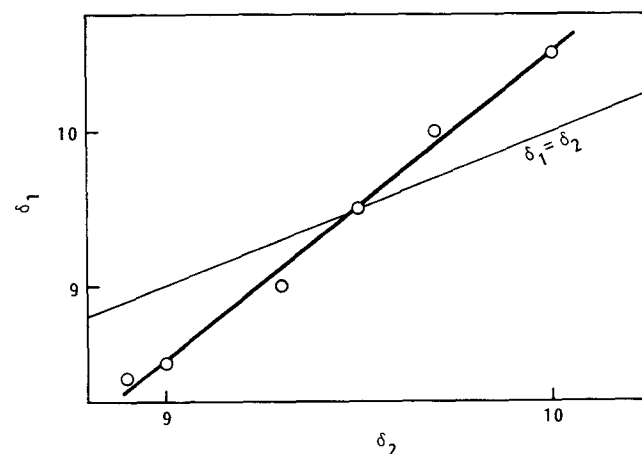
Tables 2 and 3, respectively. The apparent solubility parameters δ_2' of PAS and PHS were calculated by equation (7) and cited in the last column in Tables 2 and 3.

Figures 3 and 4 show the correlation of δ_1 versus δ_2' for PAS and PHS, respectively. The values of δ_2' for PAS and PHS were determined at zero non-solvent concentration, at which the relationship $\delta_2 = \delta_1 = \delta_2'$ should be consistent in equation (7) and the values of $10.7 (\text{cal cm}^{-3})^{1/2}$ for PAS and of $9.5 (\text{cal cm}^{-3})^{1/2}$ for PHS are obtained.

In general, the kind of the intermolecular force acting in a polymer can be presumed by the nature of the liquids in which the polymer is soluble. However, in these single solubility parameter approaches, it is not so easy for us to gain insight into the kind of intermolecular forces.

A useful method of comparing the solubility properties has been proposed by Hansen^{6,10-12} who developed the three dimensional solubility parameters approach. This method has been used for the purpose of analysing the contribution of intermolecular forces to the solubility parameter in materials. The three dimensional solubility parameter approach is based on the division of intermolecular forces into contributions from dispersion forces, dipole forces and hydrogen-bonding forces.

According to Hansen^{6,10-12}, the original Hildebrand solubility parameter is related to these parameters by the

**Figure 3** Determination of the solubility parameter δ_2 for PAS by turbidimetric measurements**Figure 4** Determination of the solubility parameter δ_2 for PHS by turbidimetric measurements

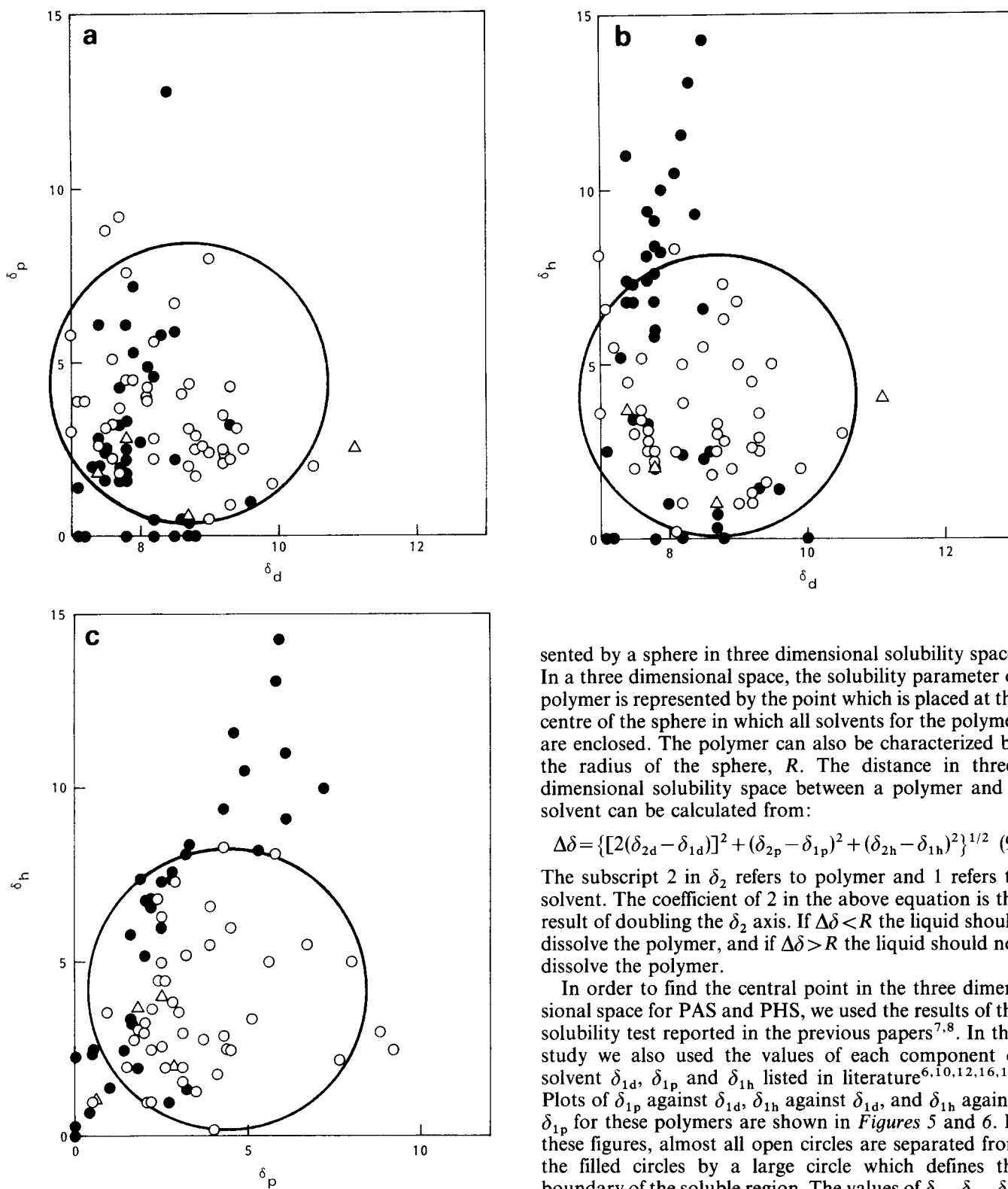


Figure 5 Solubility of PAS in diluents, soluble (○), swollen (△) and insoluble (●): (a) δ_{1p} versus δ_{1d} ; (b) δ_{1h} versus δ_{1d} ; (c) δ_{1h} versus δ_{1p}

relationship:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (8)$$

where δ is the usual solubility parameter, δ_d , δ_p and δ_h are the dispersion, the polar and the hydrogen-bonding components of the solubility parameter, respectively. Hansen^{6,10-12} has found empirically that if the δ_d axis is doubled, most polymer solubility regions can be represented by a sphere in three dimensional solubility space.

In a three dimensional space, the solubility parameter of polymer is represented by the point which is placed at the centre of the sphere in which all solvents for the polymer are enclosed. The polymer can also be characterized by the radius of the sphere, R . The distance in three-dimensional solubility space between a polymer and a solvent can be calculated from:

$$\Delta\delta = \{[2(\delta_{2d} - \delta_{1d})]^2 + (\delta_{2p} - \delta_{1p})^2 + (\delta_{2h} - \delta_{1h})^2\}^{1/2} \quad (9)$$

The subscript 2 in δ_2 refers to polymer and 1 refers to solvent. The coefficient of 2 in the above equation is the result of doubling the δ_2 axis. If $\Delta\delta < R$ the liquid should dissolve the polymer, and if $\Delta\delta > R$ the liquid should not dissolve the polymer.

In order to find the central point in the three dimensional space for PAS and PHS, we used the results of the solubility test reported in the previous papers^{7,8}. In this study we also used the values of each component of solvent δ_{1d} , δ_{1p} and δ_{1h} listed in literature^{6,10,12,16,17}. Plots of δ_{1p} against δ_{1d} , δ_{1h} against δ_{1d} , and δ_{1h} against δ_{1p} for these polymers are shown in Figures 5 and 6. In these figures, almost all open circles are separated from the filled circles by a large circle which defines the boundary of the soluble region. The values of δ_{2d} , δ_{2p} , δ_{2h} and R are determined by a trial and error method from these figures. The values of each component of the solubility parameter of PAS and PHS thus obtained are shown in Table 4. These values, substituted in equation (8), give $\delta_2 = 10.6$ (cal cm⁻³)^{1/2} for PAS and 12.0 (cal cm⁻³)^{1/2} for PHS. R was estimated to be 4.0 and 5.3 for PAS and PHS, respectively.

The values of R for PAS and PHS are comparable with other linear polymers as is shown by the points in Figure 7 which was cited in ref. 16.

Next we calculated δ_2 values using the method of Small³ and Hoy⁴ who have derived additive molar

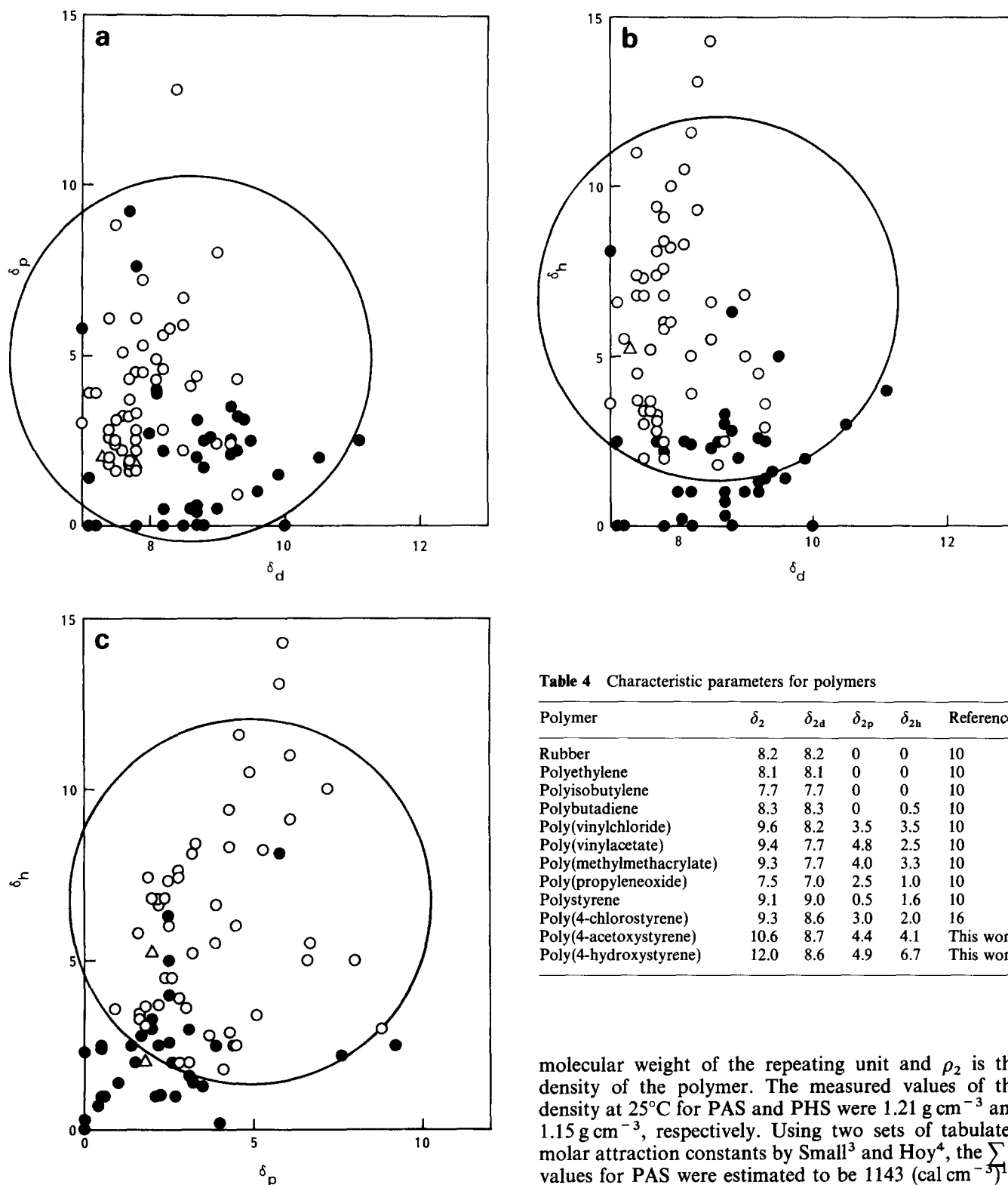


Figure 6 Solubility of PHS in diluents, soluble (○), swollen (△) and insoluble (●): (a) δ_{1p} versus δ_{1d} ; (b) δ_{1h} versus δ_{1d} ; (c) δ_{1h} versus δ_{1p}

attraction constants for various functional groups from the heat of vaporization and vapour pressure measurements on volatile substances. These methods are based on the assumption that the cohesive energy is an additive property.

According to Small³

$$\delta_2 = \rho_2 \sum F/M \quad (10)$$

where F is the group attractive constant, M is the

Table 4 Characteristic parameters for polymers

Polymer	δ_2	δ_{2d}	δ_{2p}	δ_{2h}	Reference
Rubber	8.2	8.2	0	0	10
Polyethylene	8.1	8.1	0	0	10
Polyisobutylene	7.7	7.7	0	0	10
Polybutadiene	8.3	8.3	0	0.5	10
Poly(vinylchloride)	9.6	8.2	3.5	3.5	10
Poly(vinylacetate)	9.4	7.7	4.8	2.5	10
Poly(methylmethacrylate)	9.3	7.7	4.0	3.3	10
Poly(propyleneoxide)	7.5	7.0	2.5	1.0	10
Polystyrene	9.1	9.0	0.5	1.6	10
Poly(4-chlorostyrene)	9.3	8.6	3.0	2.0	16
Poly(4-acetoxystyrene)	10.6	8.7	4.4	4.1	This work
Poly(4-hydroxystyrene)	12.0	8.6	4.9	6.7	This work

molecular weight of the repeating unit and ρ_2 is the density of the polymer. The measured values of the density at 25°C for PAS and PHS were 1.21 g cm⁻³ and 1.15 g cm⁻³, respectively. Using two sets of tabulated molar attraction constants by Small³ and Hoy⁴, the $\sum F$ values for PAS were estimated to be 1143 (cal cm⁻³)^{1/2} and 1504 (cal cm⁻³)^{1/2} respectively, and those for PHS to be 989 (cal cm⁻³)^{1/2} and 1201 (cal cm⁻³)^{1/2} respectively. The calculated values of δ_2 of PAS and PHS with both sets of data are shown in Table 5.

Finally the δ_2 values for PAS and PHS were calculated by Fedors' method⁵. This method of estimating δ_2 , which is also based on group additive constants, requires only a knowledge of the structural formula of the compound. For estimating both ΔE_v and V Fedors⁵ assumed the following equations:

$$\Delta E_v = \sum_i \Delta e_i \quad (11)$$

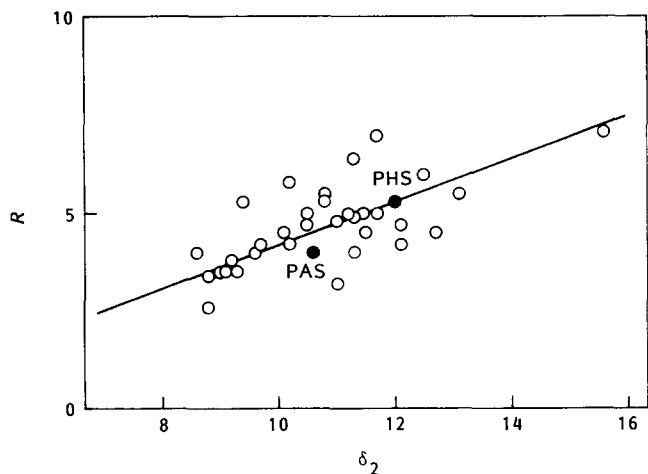


Figure 7 The relationship between R and δ_2 . Filled circles denote that of PAS and PHS

and

$$V = \sum_i \Delta v_i \quad (12)$$

where the Δe_i and Δv_i are the additive atomic and group contribution for the energy of vaporization and molar volume, respectively. Using equations (11) and (12), the solubility parameter can be written:

$$\delta = (\Delta E_v/V)^{1/2} \quad (13)$$

This method requires only a knowledge of the chemical structure in order to estimate the solubility parameter. Using Fedors⁵ tabulated data, the ΔE_v and V values for PAS are evaluated to be $15055 \text{ cal mol}^{-1}$ and $119 \text{ cm}^3 \text{ mol}^{-1}$, and for PHS $16750 \text{ cal mol}^{-1}$ and $77.5 \text{ cm}^3 \text{ mol}^{-1}$, respectively. The calculated values of δ_2 for PAS and PHS using equation (13) are shown in Table 5.

DISCUSSION

The solubility parameters of PAS and PHS obtained by three experimental methods: viscometric, turbidimetric and solubility, and those obtained by three calculation methods: those of Small³, Hoy⁴ and Fedors⁵, are summarized in Table 5. As is seen in this table, the solubility parameters of PAS obtained by various methods in this study agree quite well except for those obtained by the method of Small³ which seem to be somewhat smaller than the others. On the other hand, the solubility parameters of PHS scatter considerably. The values of δ_2 for PHS obtained by Suh and Clarke's² turbidimetric method seem to be too small. It should be noted that in this case, we could not find suitable precipitant which has sufficiently high solubility parameters, so the value of δ_2 by this method could not avoid some ambiguity. The value of $14.7 \text{ (cal cm}^{-3})^{1/2}$ for PHS estimated by the Fedors method⁵ seems to be too high. This may be attributed to the fact that the value of molar volume calculated by equation (12) is too small compared with the experimental value and that of Δe_i for the hydroxyl group is estimated to be too high.

For the purpose of comparison, we estimated the value of δ_2 for polystyrene by the turbidimetric measurements.

The precipitants used were hexane and methanol. They had higher and lower solubility parameters, respectively. The value of $\delta_2 = 8.9 \text{ (cal cm}^{-3})^{1/2}$ is obtained. This result is in good agreement with the values obtained by Cowie¹⁸ and Suh and Clarke². We also calculated the value of δ_2 for polystyrene by the methods of Small³, Hoy⁴ and Fedors⁵. These values are shown in Table 5.

For polystyrene, the δ_2 values obtained by the experimental methods are in good agreement with each other and they agree with those of the calculation method proposed by Small³ rather than those by Hoy⁴ and Fedors⁵. However, for PAS and PHS, the value obtained by the method of Small³ is distinctly lower than those obtained by the other methods. It may be considered that for non-polar polymers the δ_2 values obtained by the experimental methods agree well with that calculated using Small's data³, but for polar polymers the δ_2 values obtained by experimental methods agree instead with those calculated using Hoy's data⁴.

The turbidimetric measurements in the method of Suh and Clarke² are restricted to selection of the suitable solvent-nonsolvent systems. Therefore, it may be stated that the use of this method for the study of polar polymers such as PHS is not suitable.

As is seen in Table 4, the δ_2 value of PHS is very large compared with those of other ordinary linear polymers. This will show that there are very strong interactions between segments of PHS molecules. However, the δ_2 value of PAS is also considerable, showing that there is also strong special interaction between segments.

Hansen's three dimensional solubility parameter concept is useful to make clear the nature of such strong interactions. In Table 4 the three components of δ_2 of PAS, PHS, as well as the other representative linear polymers, are shown. As is seen in this table, the values of δ_{2d} component which is related to the dispersion force are almost the same for both PAS and PHS. In addition, they are nearly the same as those of polystyrene and poly(4-chlorostyrene) showing that the effects of dispersion force between polymer segments are the same among polystyrene derivatives. Next, values of δ_{2p} for non-polar polymers such as rubber, polyethylene, polyisobutylene and polybutadiene and polystyrene are, as expected, zero or almost zero, but they are $4.4 \text{ (cal cm}^{-3})^{1/2}$ and $4.9 \text{ (cal cm}^{-3})^{1/2}$ for PAS and PHS, respectively. It is interesting that the values of δ_{2p} for PAS and PHS are almost the same as those of poly(vinylacetate) and poly(methylmethacrylate). Finally, values of δ_{2h} for PAS and, especially, PHS are exceptionally large when compared with those of other polymers. This large value of δ_{2h} for PHS represents the result of hydrogen-bonding ability arising from the presence of hydroxyl groups. In relation to the hydrogen-bonding component, which represents the donor-acceptor character of the polymer, Yoshida *et al.*¹⁹ have found that enthalpy relaxation in PHS depends on

Table 5 Solubility parameters of polystyrene, PAS and PHS obtained from various methods

Polymers	Mangaraj ¹	Suh and		Small ³	Hoy ⁴	Fedors ⁵
		Clarke ²	Hansen ⁶			
Polystyrene	8.7*	8.9	9.1*	9.1	10.3	10.6
PAS	11.1	10.7	10.6	8.5	11.2	11.2
PHS	11.7	9.5	12.0	9.5	11.5	14.7

* Values cited from the literature^{1,10}

the formation of hydrogen bonds between hydroxyl groups which act to restrict the segmental motion of the main chain. The large value of δ_{2h} evaluated for PAS can not be explained by the formation of hydrogen bonding alone. However, it should be noted that the value is comparable to that of poly(methylmethacrylate) and poly(vinylchloride).

CONCLUSIONS

In a previous paper⁷, it was shown that isopropyl acetate and butyl acetate are theta solvents for PAS at 19.7°C and 26.8°C, respectively. In general, theta solvents exist at the limiting area of the soluble region¹⁶. As expected, the points in Figure 5 corresponding to these solvents are situated near the periphery of the soluble region represented by a circle. It may be concluded that Hansen's three dimensional solubility parameter could give three factors of solubility of PAS and PHS over a reasonable range of values.

On the other hand, none of the existing theories of the solubility parameter can explain the negative value of χ_h (or κ_1) of PHS. The values of χ_h or κ_1 for PAS and PHS are previously shown⁸ by the analysis of data of temperature variation of the limiting viscosity numbers in various solvents. As a result, it was shown that the values of κ_1 are positive for PAS in many solvents and are negative for PHS in all solvents measured, i.e. the heat of solution for PHS is shown to be negative.

When the contribution of κ_1 is endothermic, equation (3) is applicable without difficulty. However, when the contribution of κ_1 is exothermic, as in PHS in various solvents, equation (3) could not be used. Cowie *et al.*¹⁸ and Guthrie *et al.*²⁰ have assumed that the equation can be extended to exothermic systems and have estimated the value of δ_2 from:

$$\delta_2 = \delta_1 \pm (RT|\kappa_1|/V_1)^{1/2} \quad (14)$$

where $|\kappa_1|$ is taken as an absolute value. This assumption allows both positive and negative values of κ_1 to be considered. The values of δ_2 obtained from equation (14)

are 10.4 (cal cm⁻³)^{1/2} and 10.0 (cal cm⁻³)^{1/2} for PAS and PHS, respectively. The former is close to the values listed in Table 5, but the latter is somewhat smaller.

Patterson²¹ has reported that the solubility parameter theory can be correlated with the corresponding state theory. However, Patterson's²¹ theory does not explain the incompatibility of the negative value of κ_1 and the solubility parameter. It would be necessary to add the complementally additional term which explains the polymer/solvent special interaction in PHS-solvent systems.

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