

Solubility Parameters of Poly(4-substituted α -acetoxystyrenes) and Alternating Copolymers of Vinylidene Cyanide with Substituted Styrenes

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SYNOPSIS

The δ solubility parameters of three families of polymers have been determined by two calculation methods suggested by Small and Hoy. Hansen's model has also been used to assess δ and its components δ_{d0} , δ_{p0} , and δ_{h0} , so as to obtain more information on the intensity of the forces between the chain segments. Knowing the microstructure, the tacticity, and the thermal behavior of the copolymers has made it possible to explain both the different values of δ and the progression of solubility areas. Using Teas' method has made it possible to visualize on the same map the influence of the forces of interaction. This representation shows that the presence of the vinylidene cyanide unit in styrenic chains implies an increase of δ_p and a decrease of δ_d , whereas δ_h remains roughly constant for the corresponding homopolymer. © 1994 John Wiley & Sons, Inc.

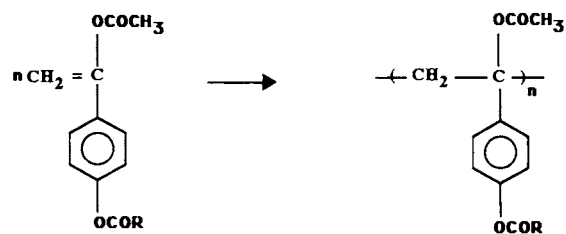
INTRODUCTION

The determination of dielectric, piezoelectric, and pyroelectric characteristics is generally carried out with thin films obtained after evaporation of the solvent. The quality of the films depends on the nature of the solvent and its evaporation rate. Using this solvent also depends on the knowledge of the parameters of the solubility of the polymer and on the intensity of interaction forces between the chain segments. Among the various theories of the solubility of polymers, Hansen's theory^{1,2} gives more information than does any of the others. For weakly polar polymers, the theory of regular solutions developed by Hildebrand³ can be applied. This theory is not valuable for polymers likely to be linked by a hydrogen bond.

To avoid this drawback, parametric models have been proposed with, most times, bidimensional or tridimensional graphic representations.^{1,2,4-6} The calculation methods proposed by Small⁷ and Hoy⁸ have been employed as well as Hansen's² model to

determine both δ solubility parameters and their components. The influence of the various grafted radicals on styrenic units, the interaction forces, and the solubility areas will be displayed with Teas'⁹ triangular representation. These theories can be summarized as follows:

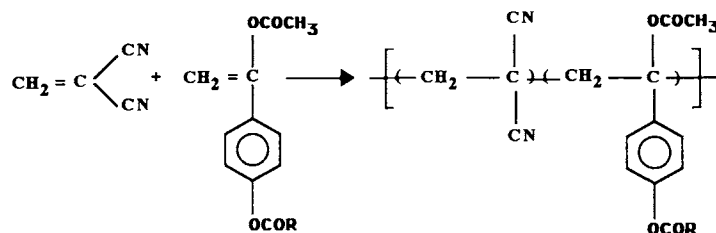
According to Hansen,¹ the density of the cohesion energy of a liquid includes all the intermolecular forces: δ_d = dispersion force; δ_p = polarity force; δ_h = hydrogen bond force; and $\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2}$. Bringing δ_d , δ_p , and δ_h in a tridimensional system and doubling the axis of δ_d , all the solvents that solubilize the polymer would be in a solubility sphere



R = CH₃, C₂H₅, nC₃H₇, OCH₃

Scheme 1 Syntheses of the polymers (A).

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R = CH₃, C₂H₅, nC₃H₇, OCH₃

Scheme 2 Syntheses of the copolymers (B).

of R_{A0} radius. The solubility parameter of a polymer is represented by a point situated in the center of this sphere and its coordinates are δ_{d0} , δ_{p0} , and δ_{h0} . The R_A distance from the center of the solubility sphere to the position of a solvent with coordinates δ_d , δ_p , and δ_h is given by

$$R_A = \sqrt{4(\delta_{d0} - \delta_d)^2 + (\delta_{p0} - \delta_p)^2 + (\delta_{h0} - \delta_h)^2}$$

If R_A is smaller than R_{A0} , the solvent is to solubilize the polymer. Considering how difficult it is to make a tridimensional representative, Hansen² used bidimensional representations, making one of the three variables unchangeable for the understanding of the results. Each time, this implies for a given polymer three bidimensional representations. To determine the solubility parameters of the polymers, copolymers, and their components, we used the δ values δ_d , δ_p , and δ_h of the various solvents given by different authors.^{1,2,10-12} A very simple method, which enables us to study the influence of the three interaction forces at the same time and to differentiate the behaviors of the apolar solvents (alkanes, aromatics, carbon tetrachloride, etc.), was proposed by Teas.⁹ To turn from Hansen's¹ tridimensional representation to the bidimensional representation, the following equations can be used:

$$F_d = 100 \frac{\delta_d}{\delta_d + \delta_p + \delta_h} \text{ (dispersion force)}$$

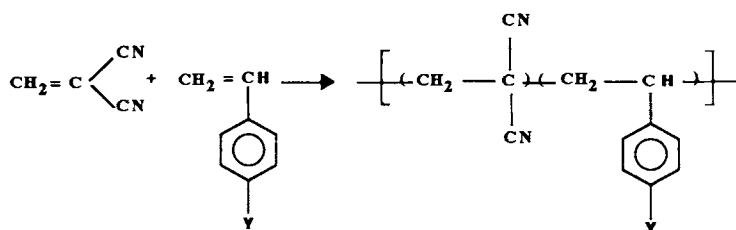
$$F_p = 100 \frac{\delta_p}{\delta_d + \delta_p + \delta_h} \text{ (polarity force)}$$

$$F_h = 100 \frac{\delta_h}{\delta_d + \delta_p + \delta_h} \text{ (hydrogen-bond force)}$$

In an equilateral triangle of sides F_d , F_p , and F_h , every solvent is represented by a point. The solvent points inside the solubility area solubilize the polymer. The best solvent is, therefore, in the center of the solubility area. Finally, it is possible to calculate the solubility parameter of the various homopolymers or alternating copolymers using the molar attraction constants of different units that are given by Small⁷ and Hoy⁸:

$$\delta = \frac{d \times \sum F}{M}$$

in which d is the polymer density; $\sum F$, the sum of molar attraction constants of various groups of the iteration unit; and M , the molar mass of the iteration unit.



Y = Cl, F, CH₂Cl, OCOCH₃

Scheme 3 Syntheses of the copolymers (C).

EXPERIMENTAL

Syntheses of the Monomers

Vinylidene cyanide (VCN) was synthesized according to a modification procedure described by Russian chemists.¹³ *Para*-substituted esterified α -acetoxy-styrenes were synthesized by heating corresponding substituted acetophenones with isopropenyl acetate.

4-Substituted styrenes are commercially available (Janssen Chemica) and were distilled before use.

Preparations of Poly(4-substituted α -acetoxy-styrenes)

These polymers (A) were prepared according to a previously described method¹⁴ (Scheme 1). Their weight-average masses M_w are in the range $30 \cdot 10^4$ – $50 \cdot 10^4$.

Table I Solubility Tests (+ Soluble; – Insoluble)

Solvent	Polymers (A)	Copolymers (B)	Copolymers (C)		
			Y = CH ₂ Cl	Y = Cl or F	Y = OCH ₃
Water	–	–	–	–	–
Glycerol	–	–	–	–	–
Methanol	–	–	–	–	–
Ethanol	–	–	–	–	–
<i>n</i> -Propanol	–	–	–	–	–
<i>n</i> -Butanol	–	–	–	–	–
Ethylene glycol	–	–	–	–	–
Benzene	+	–	–	–	–
Toluene	+	–	–	–	–
<i>m</i> -Xylene	+	–	–	–	–
Cyclohexane	–	–	–	–	–
Hexane	–	–	–	–	–
Chlorobenzene	+	+	–	–	–
1,2-Dichlorobenzene	+	+	–	–	–
Chloroform	+	+	–	–	–
Dichloromethane	+	+	+	–	–
Dichloroethylene	+	+	+	–	–
Carbon tetrachloride	–	–	–	–	–
Nitrobenzene	+	+	+	+	+
Nitromethane	+	+	+	+	+
Acetonitrile	+	+	+	+	+
DMF	+	+	+	+	+
DMSO	+	+	+	+	+
THF	+	+	+	+	–
Dioxane	+	+	+	–	–
Pyridine	+	+	+	+	+
Morpholine	+	+	+	+	+
Benzaldehyde	+	+	+	+	+
Aceton	+	+	+	+	+
Methyl ethyl ketone	+	+	+	+	+
Cyclohexanone	+	+	+	+	–
Acetophenone	+	+	+	+	+
Formic acid	–	–	–	–	–
Acetic acid	+	+	–	–	–
Acetic anhydride	+	+	+	+	+
Ethyl acetate	+	+	+	+	–
Butyl acetate	+	–	–	–	–
Diethylamine	–	–	–	–	–
Diethyl ether	–	–	–	–	–

Table II Solubility Parameters δ [(cal/cm³)^{1/2} of Polymers (A) and of Copolymers (B) and (C) Estimated by the Calculation Methods Proposed by Small⁷ and Hoy⁸

	<i>R</i>	<i>PM</i> (g/mol)	<i>d</i> (g/cm ³)	Small		Hoy	
				ΣF	δ	ΣF	δ
(A)	CH ₃	220	1.2610	1746	10.01	1815.1	10.40
	C ₂ H ₅	234	1.2380	1879	9.94	1946.6	10.30
	<i>n</i> C ₃ H ₇	248	1.2230	2012	9.92	2078.1	10.25
	OCH ₃	236	1.3070	1816	10.06	1930.3	10.70
(B)	CH ₃	298	1.22	2606	10.67	2687.7	11.00
	C ₂ H ₅	312	1.21	2739	10.62	2819.2	10.93
	<i>n</i> C ₃ H ₇	326	1.20	2872	10.57	2950.7	10.86
	OCH ₃	314	1.23	2676	10.50	2802.9	10.98
Y							
(C)	Cl	216.5	1.215	1939	10.88	1954.9	10.97
	CH ₂ Cl	230.5	1.180	2072	10.61	2086.4	10.68
	F	199	1.200	1801.2	10.86	1835.2	11.06
	OCOCH ₃	240	1.210	2203	11.01	2267.8	11.43

Preparation of Vinylidene Cyanide-substituted Styrenes Copolymers (B and C)

These copolymers were prepared by heating an equimolar mixture of VCN and substituted styrene (Schemes 2 and 3) with 2% of dichloro-2,4-benzoyl peroxide as an initiator at 45°C during 24 h.¹⁵ Their weight-average masses M_w are in the range $12 \cdot 10^4$ – $42 \cdot 10^4$.

Solubility Tests

Solubility tests were carried out in 40 solvents and in several solvent–nonsolvent and nonsolvent–non-

solvent pairs. These tests were performed at 22°C; approximately 20 mg of the sample was poured in 2 mL of the solvent. All the used solvents were previously distilled.

Measurements of Densities

The (A) polymer densities were measured on film by Davenport's method with a concentration gradient and with a mixture of carbon tetrachloride and cyclohexane. For (B) and (C) copolymers, densities were measured by a picnometer on film.

Table III Solubility Parameters δ and Their Components (δ_{d0} , δ_{p0} , δ_{h0}) for Polymers

Polymer	R_{A_0}	δ	δ_{d0}	δ_{p0}	δ_{h0}	Ref.
Poly(vinyl chloride)		9.6	8.2	3.5	3.5	10 and 18
Poly(vinyl acetate)		9.4	7.7	4.8	2.5	10 and 18
Poly(methyl methacrylate)		9.3	7.7	4.0	3.3	10 and 18
Polystyrene		9.1	9.0	0.5	1.6	10 and 18
Poly(4-chlorostyrene)		9.3	8.6	3.0	2.0	11
Poly(4-acetoxystyrene)	4.0	10.6	8.7	4.4	4.1	21
Polymers (A)	4.8	10.7	8.7	5	3.6	^a
Copolymers (B)	4.4	10.7	10.5	5.5	3.5	^a
Copolymer (C) Y = OCOCH ₃	3.0	11.15	8.4	6.6	3.2	^a
Copolymers (C) Y = Cl or F	3.8	10.94	8.3	5.9	4.0	^a
Copolymer (C) Y = CH ₂ Cl	3.8	10.7	8.3	5.8	3.5	^a

^a This work.

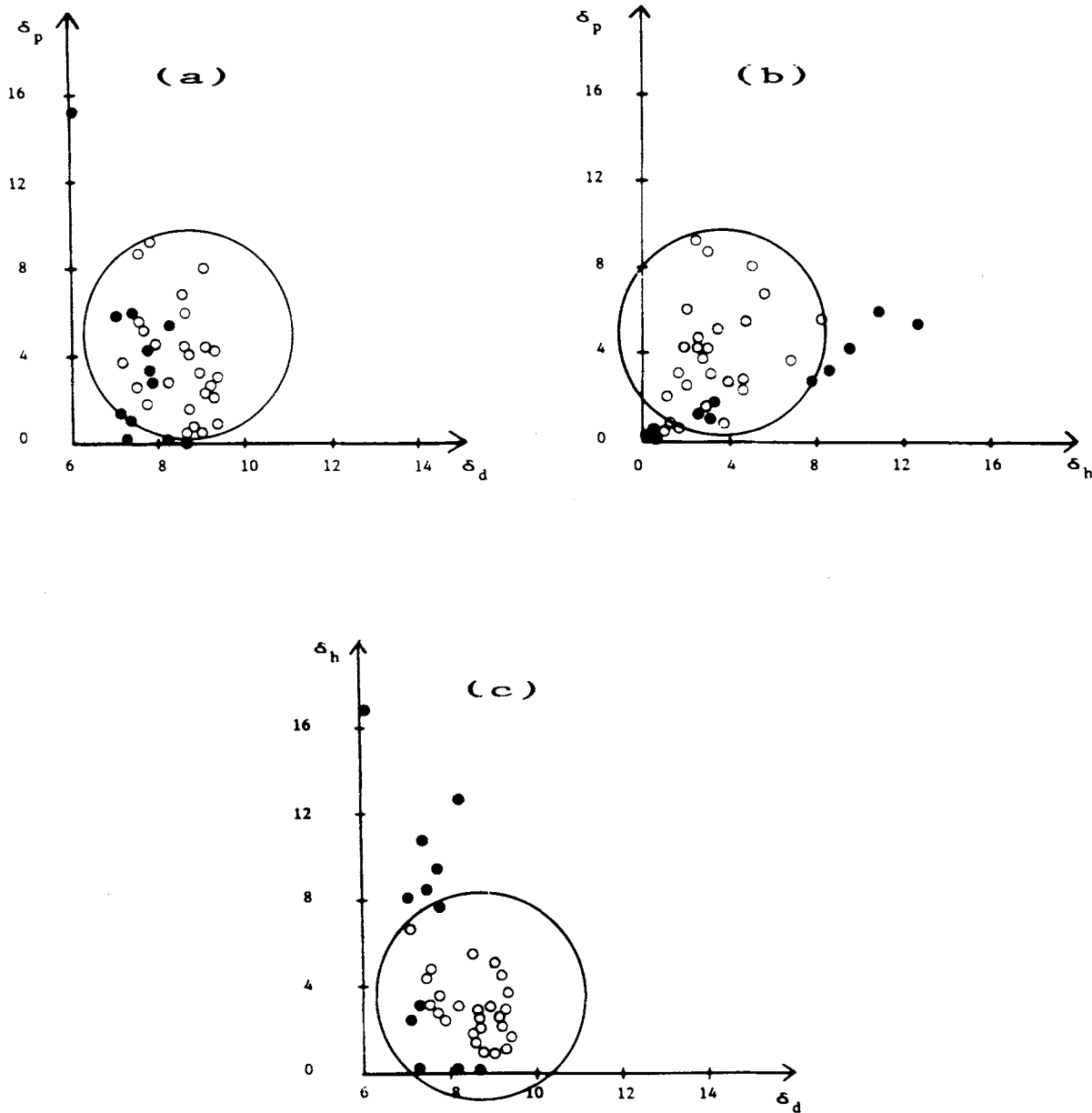


Figure 1 Solubility of polymers (A) in solvents: (○) soluble; (●) insoluble. (a) δ_p vs. δ_d ; (b) δ_p vs. δ_h ; (c) δ_h vs. δ_d .

RESULTS AND DISCUSSION

The δ solubility parameters of the various polymers or copolymers were determined by calculation methods involving molar attraction constants given by Small⁷ and Hoy.⁸ Using the parametric model of Hansen,² taking into account the different interaction forces, allowed us to evaluate the solubility parameters as well as their components (δ_{d0} , δ_{p0} , δ_{h0}) and the radii R_{A0} solubility spheres. The Teas' representation⁹ enabled us to visualize the solubility

areas and the impact of VCN and of various grafted groups onto styrenic units. First, we examine every polymer family and then we make a global survey.

Polymers (A)

Previous studies¹⁶ by ¹³C-NMR, thermogravimetry,¹⁷ and DSC have shown that these polymers have neither a glass transition temperature nor a melting point and that they degrade beyond 170°C with loss of acetic acid; moreover, they are syndiotactic in the

majority because of the steric hindrance. Solubility tests (Table I) show that these polymers are soluble in all usual solvents except for alcohols, alkanes, and carbon tetrachloride. The values of solubility parameters obtained by calculation according to the data of Small⁷ and Hoy⁸ are achieved by using the *para*-esterified α -acetoxystyrene unit and can be found in Table II. As this table highlights, these values of Small⁷ (9.9–10.1) are lower than those of Hoy⁸ (10.2–10.7). For polar polymers, studies revealed that calculated values according to the data of Hoy⁸ are in good agreement with the experimental

results. The decrease of δ for this polymer group from $\delta = 10.7$ for $R = \text{OCH}_3$ to $\delta = 10.25$ for $R = n\text{C}_3\text{H}_7$ is related to the introduction of hydrophobe methylenic groups. We found with Hansen's² method that $\delta = 10.66$ and $\delta_{d0} = 8.7$; $\delta_{p0} = 5$; and $\delta_{h0} = 3.5$; and for R_{A0} , a value of 4.8 (Table III). In comparison with other polar polymers, the poly-*para*-esterified α -acetoxystyrenes have the same values of δ_{d0} as has poly(4-acetoxystyrene), the same values of δ_{p0} as has poly(vinyl acetate), and the same values of δ_{h0} as has poly(vinyl chloride) (see Fig. 1).

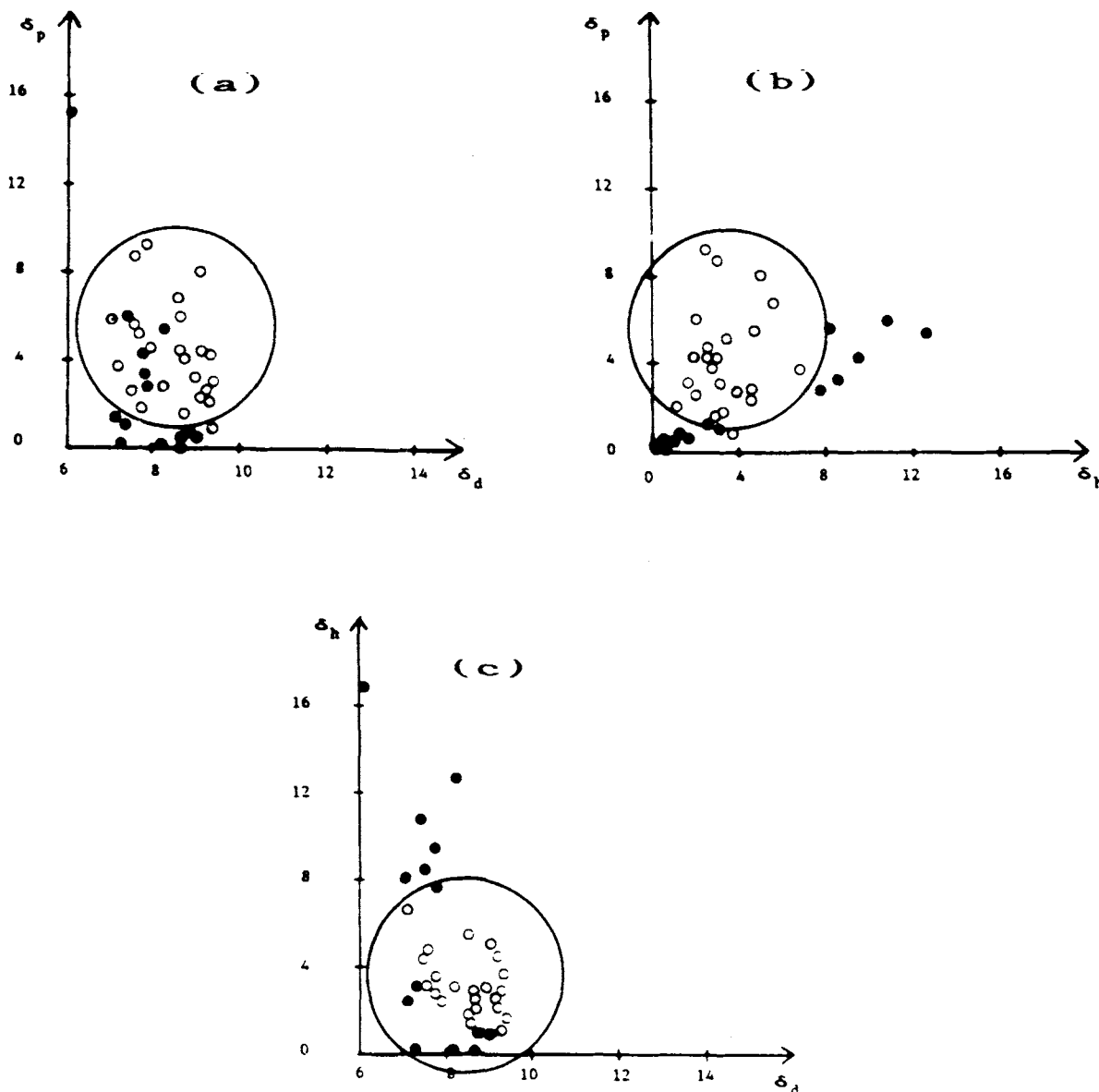


Figure 2 Solubility of copolymers (B) in solvents: (O) soluble; (●) insoluble. (a) δ_p vs. δ_d ; (b) δ_p vs. δ_h ; (c) δ_h vs. δ_d .

Polymers (B)

The copolymers of VCN with *para*-esterified α -acetoxystyrenes have neither a glass transition temperature nor a melting point and degrade close to 240°C with loss of acetic acid. The gain of temperature of 70°C is due to a decrease of the steric hindrance as compared to polymers (A).

The ^{13}C -NMR study shows that the copolymers are perfectly alternating and are mostly syndiotactic.¹⁵ For the calculation of solubility parameters,

the iteration unit is the *para*-substituted α -acetoxystyrene-VCN (see Scheme 2). The δ calculated values according to Small's⁷ and Hoy's⁸ data are detailed in Table II. As for polymers (A), the δ values calculated with Small's⁷ data (10.5–10.7) are lower than those from Hoy's⁸ data. Examination of Table I shows that copolymers (B) are soluble in the same solvents as are polymers (A) except for aromatic solvents. The application of Hansen's² model (Fig. 2) gives for these copolymers a δ value of 10.7, and for components, $\delta_{d0} = 8.5$, $\delta_{p0} = 5.5$, and $\delta_{h0} = 3.5$.

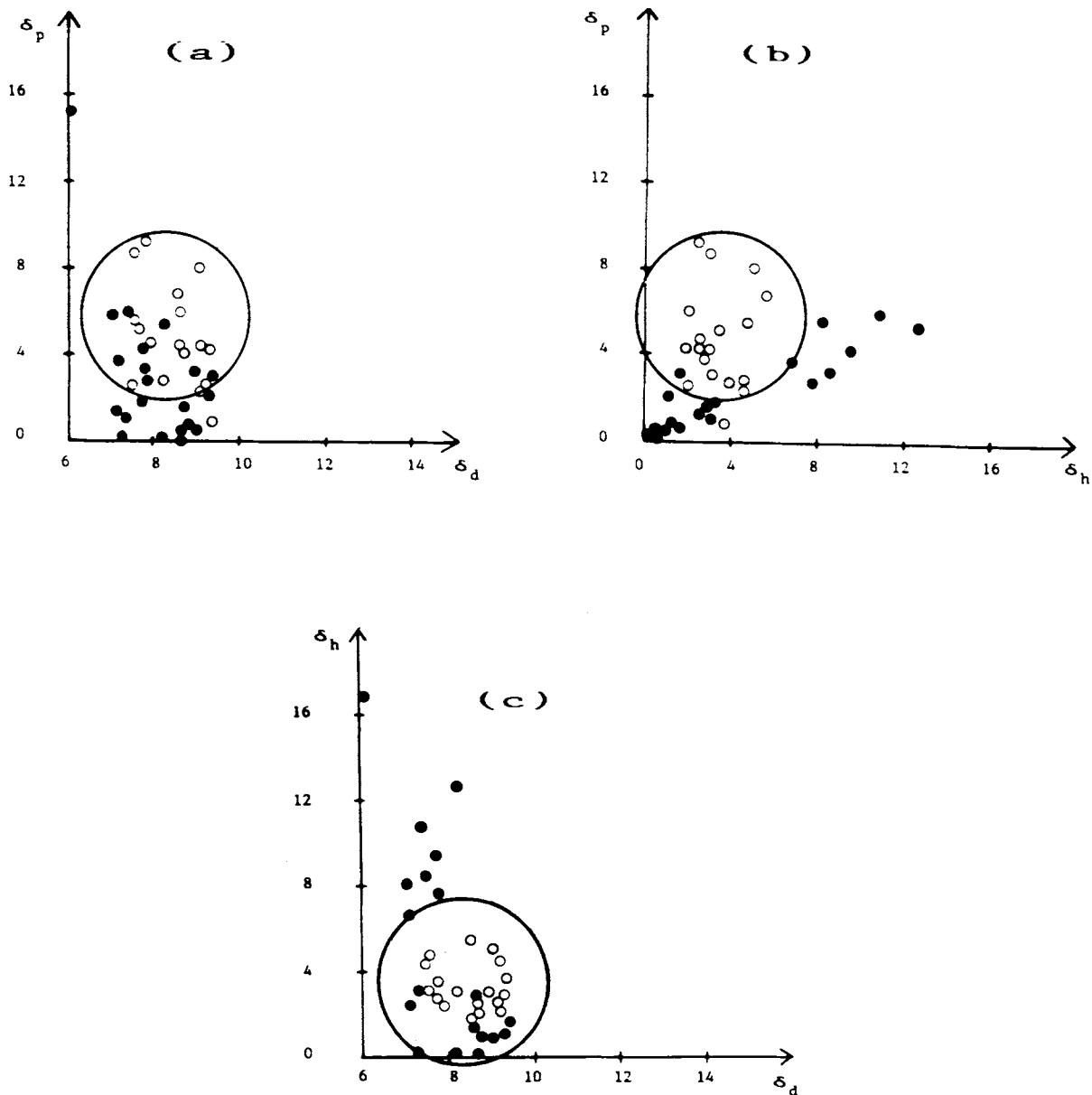


Figure 3 Solubility of copolymers (C) in solvents with $Y = \text{CH}_2\text{Cl}$: (O) soluble; (●) insoluble. (a) δ_p vs. δ_d ; (b) δ_p vs. δ_h ; (c) δ_h vs. δ_d .

The values are similar to those of homopolymers (A) with a slight increase of δ_{p0} related to the introduction of CN groups that are strongly polar. The increase of δ_{p0} remains low and the solubility spectrum remains largely different from that of the VCN-vinylacetate copolymer.¹⁸ This slight difference of solubility between polymers (A) and copolymers (B) shows that CN are masked. This can be explained with the help of the microstructure of

polymers (B) and of the molar volumes of various groups neighboring the CN substituents.

Copolymers (C)

These copolymers as compared to polymers (A) and copolymers (B) have a glass transition temperature in the range 120–180°C but no melting point.¹⁹ They degrade close to 300°C and are amorphous and more

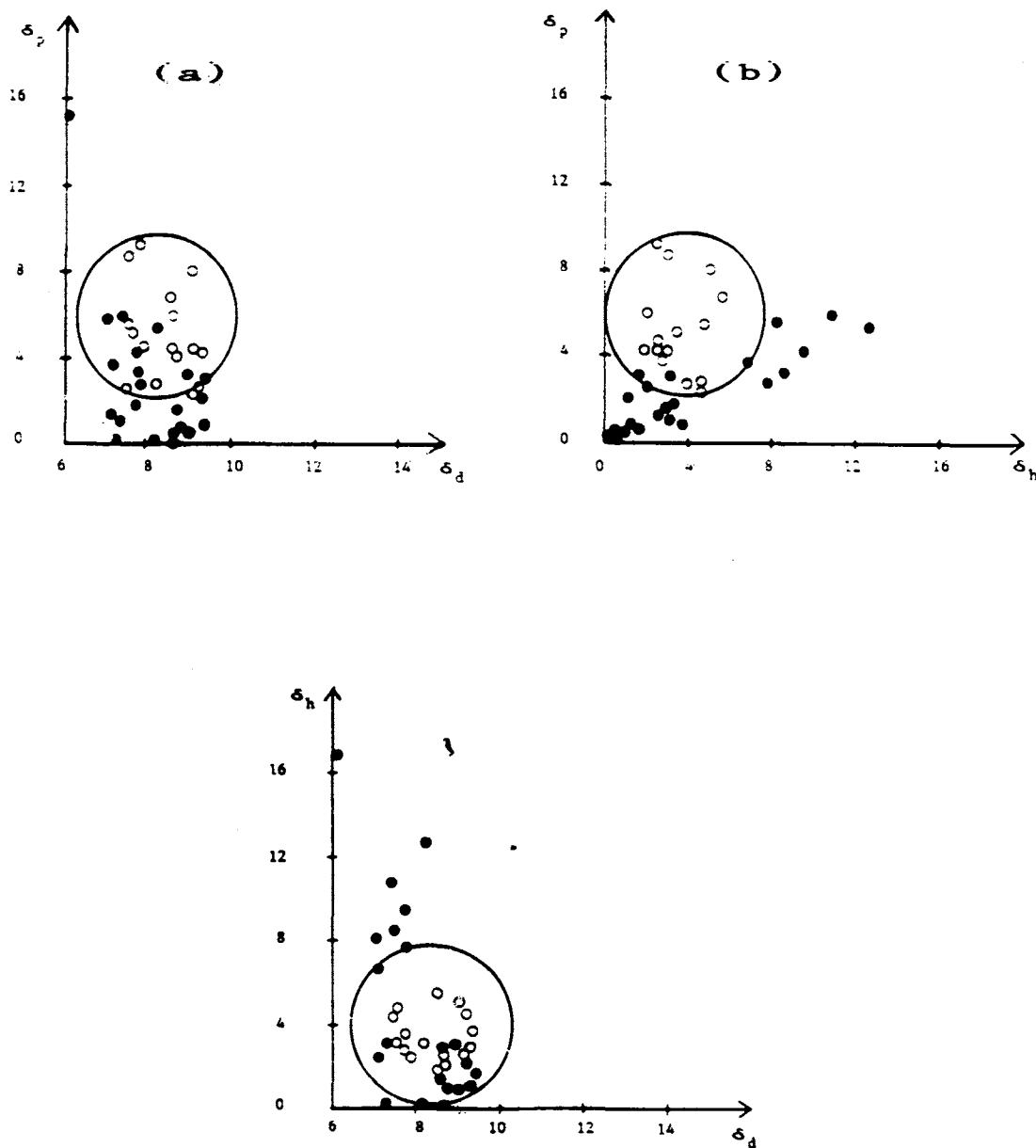


Figure 4 Solubility of copolymers (C) in solvents with Y = Cl or F: (O) soluble; (●) insoluble. (a) δ_p vs. δ_d ; (b) δ_p vs. δ_h ; (c) δ_h vs. δ_d .

stable. The ^{13}C -NMR studies²⁰ show that they are perfectly alternating. The unit 4-substituted styrene-VCN has been chosen for the calculation of the δ solubility parameters (Figs. 3-5).

The calculated values appear in Table II. As previously described, the values with Small's data⁷ are lower (10.6-11) than those according Hoy's data⁸ (10.7-11.4). Examination of Table I and of Figure 6 clearly shows that the solubility of these copolymers depends on the polarity and on the volume of the *para*-substituent of the styrenic unit. It is interesting to make a comparison between these co-

polymers (C) with copolymers (B) and the corresponding styrenic homopolymers by analyzing the values of the different interaction forces (δ_{d0} , δ_{p0} , δ_{h0}) found with Hansen's method.²¹ The lack of the acetoxy group in α of the styrenic unit in copolymers (B) implied a slight increase of δ_{p0} while the values of δ_{d0} and δ_{h0} remained similar. The comparison between copolymers (C) and poly(4-acetoxystyrene) shows that there is essentially a strong increase of δ_{p0} related to the introduction of CN groups. The examination of the values of copolymers (C) ($Y = \text{Cl}$) with those of poly(4-chlorostyrene) reveals

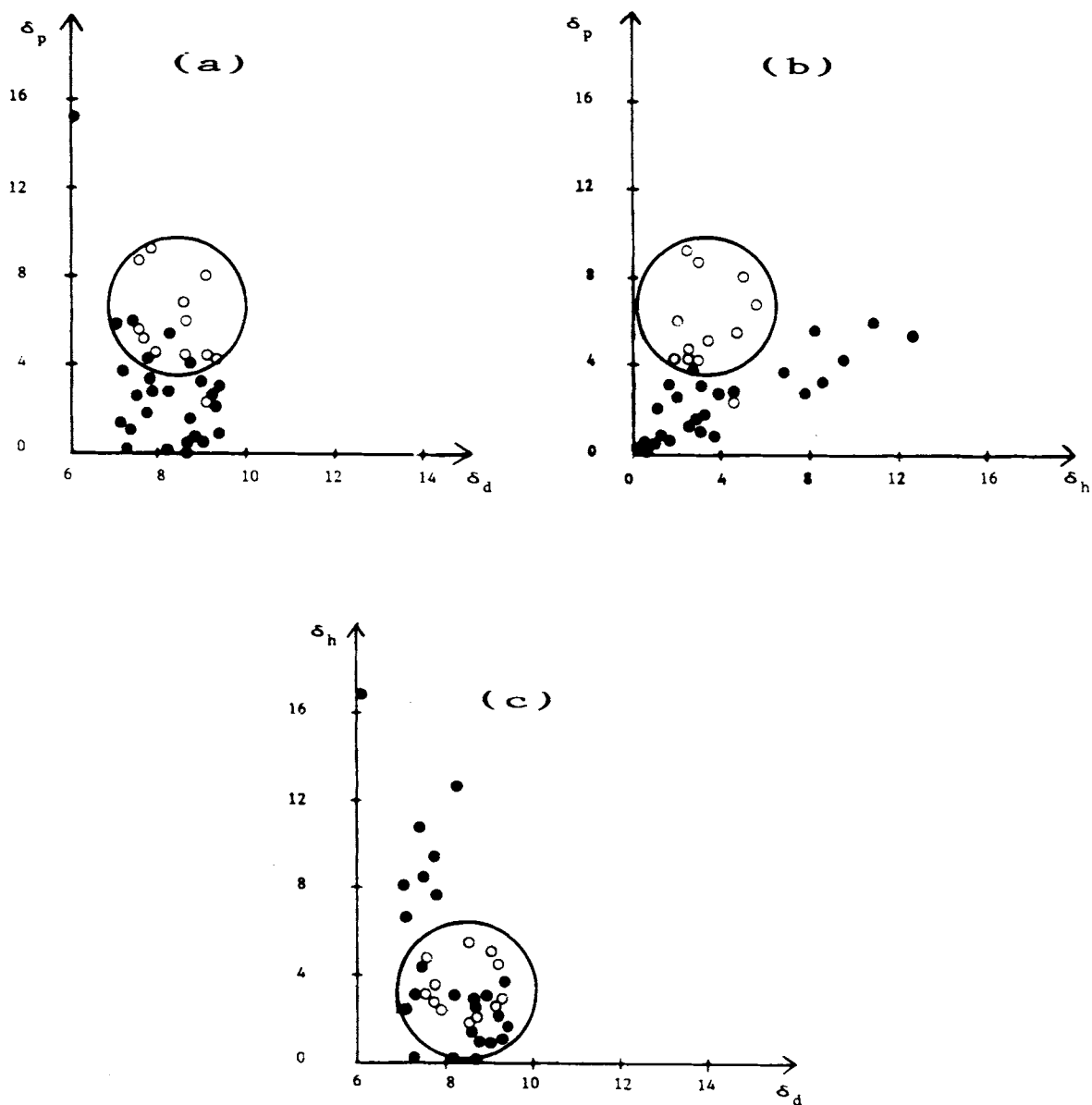


Figure 5 Solubility of copolymers (C) in solvents with $Y = \text{OCOCH}_3$: (○) soluble; (●) insoluble. (a) δ_p vs. δ_d ; (b) δ_p vs. δ_h ; (c) δ_h vs. δ_d .

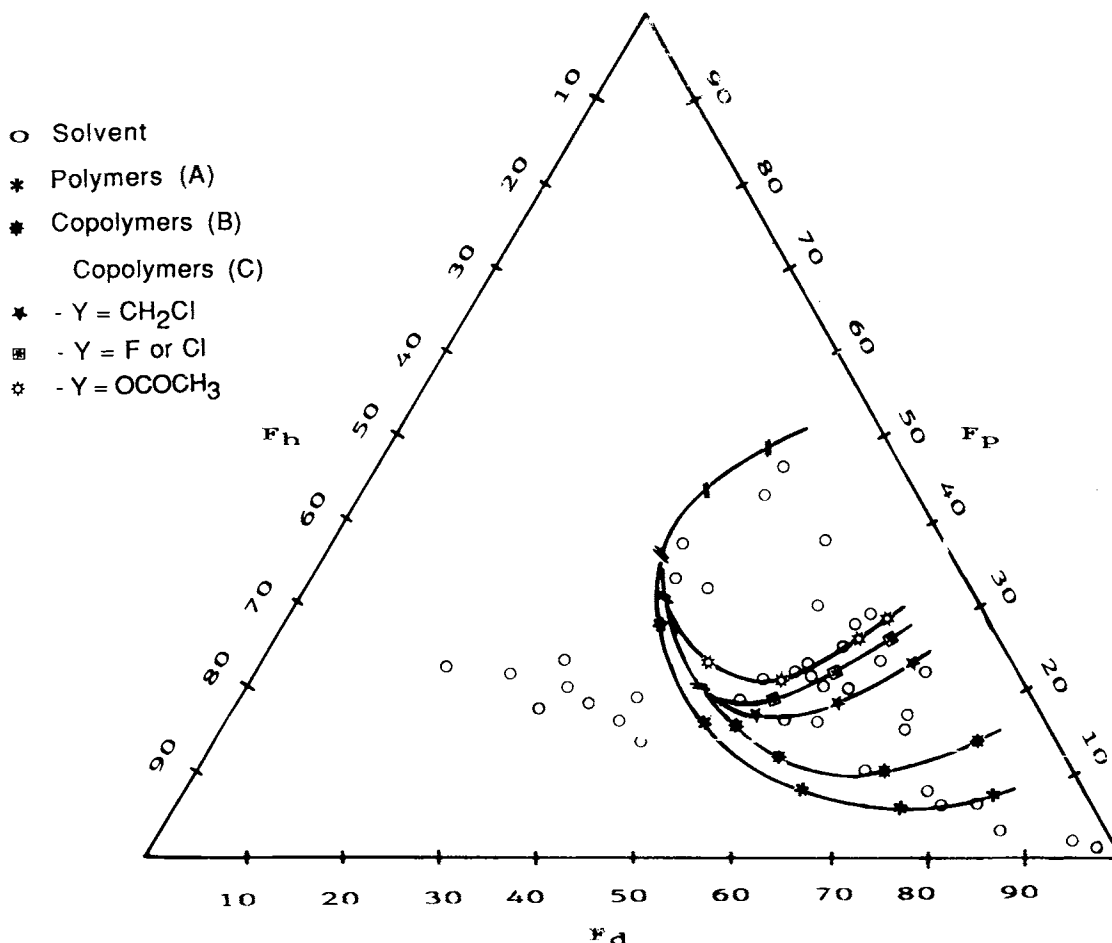


Figure 6 Teas' diagram of solubility of polymers (A) and of copolymers (B) and (C) ($Y = \text{CH}_2\text{Cl}$; F or Cl; OCOCH_3).

that the introduction of CN groups has no effect on the value of δ_{d0} , whereas there is a very important increase of δ_{p0} and δ_{h0} . It can be noticed that the value of δ_{h0} for copolymers (C) ($Y = \text{Cl}$) is similar to that of poly(vinyl chloride). The high value of δ_{p0} in these copolymers (C) and the decrease of solubility as compared to copolymers (B) show that the CN groups in copolymers (C) are more adequate to form strong dipolar interactions between the chain segments.

Finally, the Teas' representation⁹ has enabled us to demonstrate the influence of three interaction forces. Figure 6 gives the progression of the solubility areas in the different analyzed samples. It can be seen solubilities areas mostly progress in inverse direction of the polarity forces.

CONCLUSION

The solubility parameters of three polymer families have been calculated according to Small's and Hoy's

methods. The application of Hansen's model has enabled us to determine the solubility parameter δ as well as their components δ_{d0} , δ_{p0} , and δ_{h0} for the different kinds of polymers. The calculated values using Hoy's data are in good agreement with those of Hansen's model and the literature data for similar products. Contrary to the copolymer of VCN with vinyl acetate, also perfectly alternating (with a δ parameter $\delta = 11.1$), which is only soluble in DMF or DMSO, the (B) and (C) copolymers are more easily soluble in many solvents. This study revealed that a strongly polar CN group changes the δ_{p0} component compared to the corresponding styrenic homopolymer. The solubility area of a copolymer depends on the molar volumes of grafted groups on styrenic monomers and on their polarities.

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