

Solubility Behavior of an Organic Soluble Polyimide

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Synopsis

The solubility behavior of an organic soluble polyimide synthesized from 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 2,3,5,6-tetramethyl-*p*-phenylene diamine in about 60 liquids was investigated via solubility experiments. These results were put into a computer program to obtain a three-dimensional representation of the polymer solubility region in the Hansen space; the values of dispersion, hydrogen bonding, and polar components of the total solubility parameter were 10.6, 5.3, and 5.3 cal^{1/2}/cm^{3/2}, respectively, and the total solubility parameter was 12.96 cal^{1/2}/cm^{3/2} after calculation. The total solubility parameter determined from an equilibrium swelling method was between 12.9 cal^{1/2}/cm^{3/2} and 13.1 cal^{1/2}/cm^{3/2}. Both experimental results were in very good agreement. The calculated dispersion solubility parameter obtained from its correlation with the refractive index of the polymer was 10.56 cal^{1/2}/cm^{3/2} and was in accordance with the result obtained from the polymer solubility region in the Hansen space. However, the total solubility parameter of the organic soluble polyimide calculated from the Fedors method was 12.1 cal^{1/2}/cm^{3/2} and was low in comparison to the experimental results.

INTRODUCTION

The excellent thermal properties of polyimides are well known. Because of their insolubility and their high glass transition temperatures, they are difficult to fabricate and their uses are limited. In fact, most polyimides are processed in the form of their polyamic acid precursors, which are then thermally or chemically converted to the imide structure. However, several thermally stable polyimides that are soluble in organic solvents have appeared in the literature.¹⁻⁴ Harris et al.¹ suggested that the majority of approaches to organic soluble, thermally stable polyimides involved the following modification:

1. The introduction of large polar or nonpolar substituents along the backbone
2. The incorporation of flexible or kinked thermally stable linkages in the backbone
3. The disruption of symmetry or recurrence regularity through the copolymerization of two dianhydrides or two diamines

However, most efforts have been devoted to the physical properties of organic soluble polyimides, but little information was available on their solubility be-

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havior. Solubility parameter considerations have helped to solve numerous specific problems related to polymeric coatings.

The first method to determine solubility parameter was used by Beerbower et al.,⁵ who expressed the amount of hydrogen bonding energy by the hydrogen bonding number $\Delta\nu$. They plotted the data for various solvents in a diagram with the solubility parameter δ along the horizontal axis and the hydrogen bonding number $\Delta\nu$ along the vertical axis. All the solvents in which a given polymer was soluble fell within a certain region. Crowley et al.^{6,7} used an extension of this method by including the dipole moment of the solvents. However, as this involved a comparison of a number of solvents in a three-dimensional system, the method was unpractical. The second method was developed by Hansen.⁸⁻¹⁰ He experimentally determined the solubility parameters 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 dispersion (δ_d), polar (δ_p), and hydrogen bonding (δ_h) forces could be plotted on three mutually perpendicular axes. The δ_d , δ_p , and δ_h of the polymer under investigation are the coordinates of the center of the solubility region in the three-dimensional structure. The third method was proposed by Chen.¹¹ He introduced a quantity

$$X_H = \frac{V_s}{RT} [(\delta_{d,S} - \delta_{d,P})^2 + (\delta_{p,S} - \delta_{p,P})^2]$$

where the subscripts *S* and *P* denoted solvent and polymer, respectively, and V_s was the molar volume of the probe used. The solubility data were plotted in a δ_h - X_H diagram. A disadvantage of this method was that the characteristics of the polymer were estimated beforehand. Other two-dimensional methods for the representation of solubility data were the δ_p - δ_h diagram proposed by Hery¹² and the δ - δ_h diagram proposed by Hoernschemeyer,¹³ but their representation of the solubility region was not correct.

The determinations of total solubility parameter include the viscosity and equilibrium swelling methods. Mangaraj et al.¹⁴ plotted the intrinsic viscosity ($[\eta]$) against the total solubility parameters of solvents. A value of δ_t corresponding to the maximum of the $[\eta]$ vs. δ_t parabolic curve was obtained and assigned as the total solubility parameter for the polymer. This method requires some soluble solvents whose solubility parameters are close to each other and consecutive. Chapiro et al.¹⁵ and Fuehrer¹⁶ used the equilibrium swelling method to determine the total solubility parameter of polyvinyl fluoride and polyvinylidene fluoride.

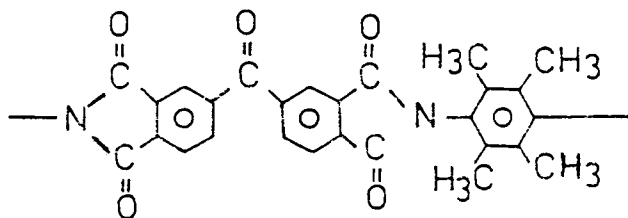
The prediction of the total solubility parameter uses the following equation:

$$\delta = \left(\frac{E_{\text{coh}}}{V} \right)^{1/2}$$

where E_{coh} was the cohesive energy and V was the molecular volume. For substances of low molecular weight, E_{coh} was considered as an additive property proposed by Dunkel¹⁷ who derived group contribution for the cohesive energy of liquids at room temperature. Hayes,¹⁸ Di Benedetto,¹⁹ Hoftyzer and Van Krevelen,²⁰ and Fedors²¹ had applied Dunkel's method to polymers. However, Fedors had more data available than other methods. Bunn²² dealt with the

cohesive energy at the boiling point, while Bondi^{23,24} investigated the cohesive energy properties at 0 K. They tried to predict the solubility parameters of low molecular weight substances at various temperatures. Other methods were the gas chromatography method used by Dipaola-Baranyi et al.²⁵ to estimate the solubility parameter of polystyrene at 193°C and poly (methyl acrylate) at 100°C and the inverse gas chromatograph method employed by Ito et al.²⁶ to estimate the solubility parameters of some olefin polymers and copolymers.

Fully imidized polyimide systems recently reported by Pfeifer and Rohde² were organic soluble polyimide. The repeating unit in one of the polyimide systems was



In this article, the solubility behavior of this organic soluble polyimide (OSPI) was studied in detail. The OSPI was first prepared by the condensation reaction of 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) with 2,3,5,6-tetramethyl-*p*-phenylene diamine (TMPD), and the cyclization was processed by chemical imidization method at the second step. In this work the solubility behavior of OSPI in about 60 liquids with known solubility parameters has been examined. From these experiments, the solubility region of the polymer in three-dimensional Hansen space⁸⁻¹⁰ was determined and the values of solubility parameters were evaluated. The total solubility parameter of the polymer has also been measured from the equilibrium swelling method¹⁵ and calculated from Fedors method.²¹ The comparison of the experimental results with the calculated results is also reported in this article.

EXPERIMENTAL

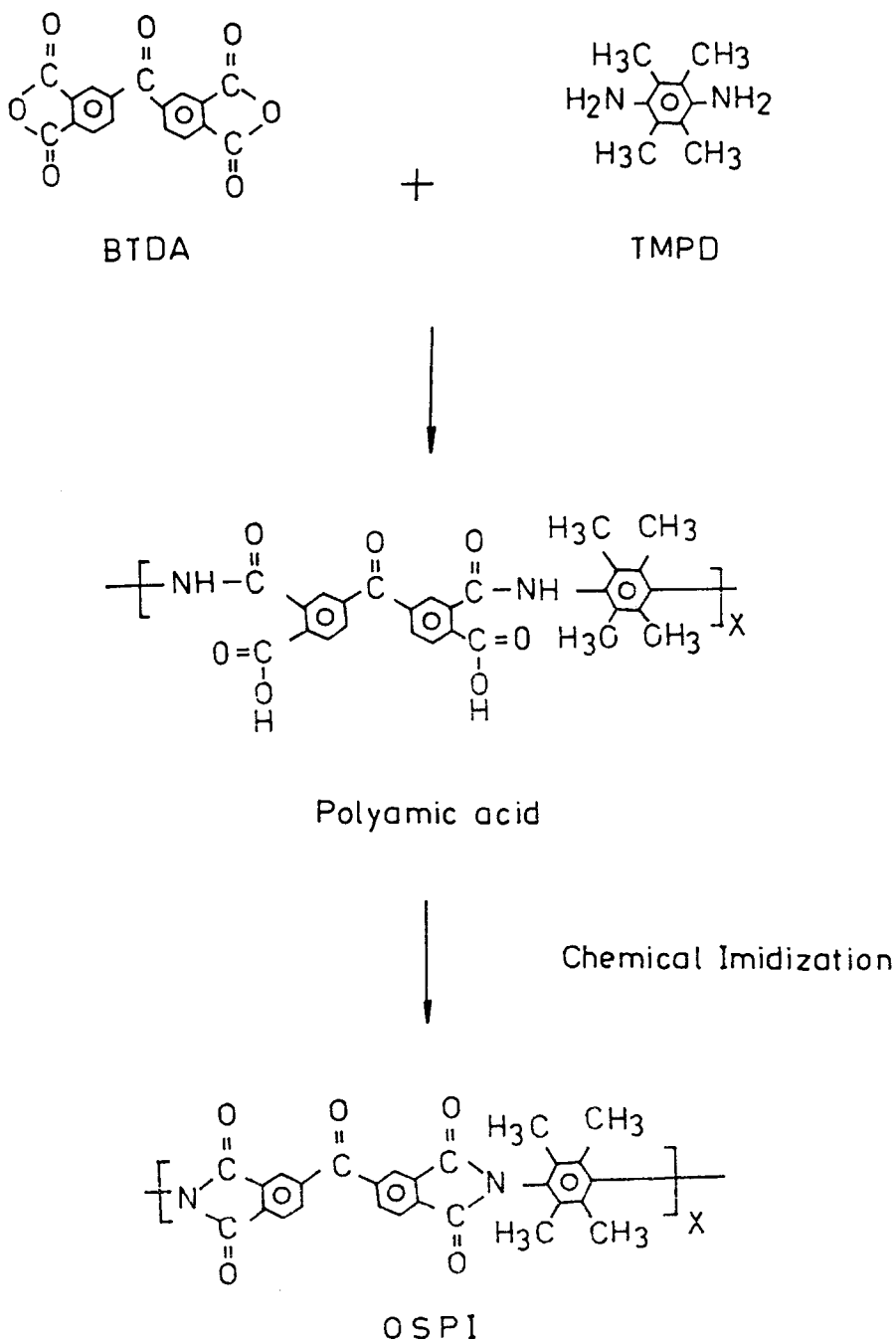
Materials

3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BTDA) (Polyscience) was recrystallized from acetic anhydride and dried under reduced pressure at 200°C before use. 2,3,5,6-Tetramethyl-*p*-phenylene diamine (TMPD) (Fluka) was recrystallized from alcohol and dried under reduced pressure. *N*-methyl-2-pyrrolidone (NMP) (Merck) was distilled before being stored in 4 Å molecular sieves. All liquids used for solubility experiments as well as for equilibrium swelling methods were of reagent grade and used without further purification.

Polyimide and Film Preparation

TMPD dissolved in NMP was taken in a reaction flask fitted with nitrogen purge system. The solution was cooled to 0°C when equivalent moles of BTDA were added to the solution with stirring. The solid content of the solution was 20%. This solution was kept at room temperature for 24 h. Thus, polyamic acid was obtained. The chemical imidization was carried out by treating the polyamic

acid in NMP with a mixture of acetic anhydride and pyridine (mole ratio of acetic anhydride : pyridine = 4 : 3.5 mol/mol polyamic acid) at 60°C for 8 h. The final solution was added to methanol dropwise so as to allow the OSPI to precipitate. Infrared spectra of the polyamic acid and polyimide were taken by using Perkin-Elmer 842 IR spectrophotometer. The intrinsic viscosity, run at 5% concentrations in NMP at 30°C, was 1.04 dL/g. The synthetic scheme is shown as follows:



To better evaluate the solubility behavior of OSPI in testing liquids, powder form of OSPI was transformed into films by the following procedures. A concentrated solution (20 wt % OSPI in NMP) was first cast at room temperature on a cleaned glass plate and then placed in a forced-ventilation oven at 200°C for 2 h to allow complete evaporation of the solvent. The final thickness of films was between 20 and 30 μm . After cooling to room temperature, the corresponding film was extracted with water overnight in a Soxhlet apparatus, vacuum dried, and cut into strips for solubility experiments.

The refractive index of the polyimide film at 25°C was experimentally evaluated to be $n_D = 1.687$.

Solubility Experiments

Solubility experiments were carried out as follows.⁸⁻¹⁰ Strips of 0.5000 ± 0.0005 g were immersed in 5 mL of liquid in sealed glass tubes. The sealed tubes were placed in a water bath at 25°C and continuously shaken for 7 days. Since few of the liquids tested were able to dissolve OSPI over the period of 7 days, the samples were also heated at 100°C for 24 h, and then cooled at 25°C for visual inspection. On the basis of their ability to dissolve or swell the polymer, the solubility extent of the liquid is classified into four categories: solvent (S), good swelling agent (GSA), poor swelling agent (PSA), and nonsolvent (NS). Table I lists the liquids used and their extent of solubility.

Equilibrium Swelling Method

The equilibrium swelling method was carried out as follows.¹⁵ Strips weighing 0.035–0.055 g were immersed in a glass tube that contained the liquid under investigation. The tubes were placed in a water bath kept at $25.0 \pm 0.5^\circ\text{C}$. The film was removed from the liquid after equilibrium swelling was reached (about 1 h), pressed lightly between two sheets of filter papers, placed in a tapered flask, and weighed. The "equilibrium swelling ratio" expressed in percent was calculated according to eq. (1).

$$\text{Equilibrium swelling ratio} = (W_s - W_0)/W_0 \times 100\% \quad (1)$$

where W_s is the weight of the swollen film and W_0 is the dry weight of the film.

RESULT AND DISCUSSION

Imidization Reaction Characterized by IR Spectra

The infrared spectra of polyamic acid and OSPI are shown in Figure 1. In spectrum (a), which corresponds to polyamic acid, the absorption band in the range of $3100\text{--}3300\text{ cm}^{-1}$ is due to the stretching of O—H, and the absorption band at 1660 cm^{-1} is secondary amide groups. In the spectrum (b), which represents the OSPI structure, the absorption bands at 1780 and 1730 cm^{-1} are related to symmetry and asymmetry of C=O of imide group, respectively, while the absorption bands at 1100 and 720 cm^{-1} are the vibrations of imide structure. In comparison, the disappearances of absorption bands at $3100\text{--}3300$ and 1660 cm^{-1} and the appearances of absorption bands at 1780 , 1730 , 1100 , and 720 cm^{-1} in Figure 1 indicate a rather complete imidization.

TABLE I
Solubility Parameters ($\text{cal}^{1/2}/\text{cm}^{3/2}$)²⁷ of Liquids and Extent of Solubility of OSPI

No.	Liquid	$\delta_{d,P}$	$\delta_{p,P}$	$\delta_{h,P}$	$\delta_{t,P}$	Extent of solubility
1.	Acetic acid	7.1	3.9	6.6	10.5	NS
2.	Acetic anhydride	7.8	5.7	5.0	10.9	GSA
3.	Acetone	7.6	5.1	3.4	9.8	NS
4.	Acetonitrile	7.5	8.8	3.0	11.9	NS
5.	Acrylonitrile	8.0	8.5	3.3	12.1	PSA
6.	Aniline	9.5	2.5	4.9	11.0	GSA
7.	Benzyl alcohol	9.0	3.1	6.7	11.6	GSA
8.	1-Butanol	7.8	2.8	7.7	11.3	NS
9.	<i>n</i> -Butyl acetate	7.7	1.8	3.1	8.5	NS
10.	Butyl cellosolve	7.8	2.5	6.0	10.2	NS
11.	Butyric acid	7.3	2.0	5.2	9.2	NS
12.	Cellosolve	7.9	4.5	7.0	11.5	NS
13.	Cellosolve acetate	7.8	2.3	5.2	9.7	PSA
14.	Chlorobenzene	9.3	2.1	1.0	9.6	PSA
15.	1-Chlorobutane	7.5	3.4	1.7	8.4	NS
16.	Chloroform	8.7	1.5	2.8	9.3	GSA
17.	<i>m</i> -Cresol	8.8	2.5	6.3	11.1	S
18.	Cyclohexanone	8.7	3.1	2.5	9.6	PSA
19.	<i>o</i> -Dichlorobenzene	9.4	3.1	1.6	10.0	NS
20.	Diethyl ether	7.1	1.4	2.5	7.7	NS
21.	Diethylene glycol	7.9	7.2	10.0	14.6	NS
22.	Diisobutyl ketone	7.8	1.8	2.0	8.3	NS
23.	<i>N,N</i> -dimethyl acetamide	8.2	5.6	5.0	11.1	S
24.	<i>N,N</i> -dimethyl formamide	8.5	6.7	5.5	12.1	S
25.	Dimethyl sulfoxide	9.0	8.0	5.0	13.0	GSA
26.	1,4-Dioxane	9.3	0.9	3.6	10.0	GSA
27.	Ethanol	7.7	4.3	9.5	13.0	NS
28.	Ethanol amine	8.4	7.6	10.4	15.4	GSA
29.	Ethyl acetate	7.7	2.6	3.5	8.8	PSA
30.	2-Ethyl hexanol	7.8	1.6	5.8	9.9	PSA
31.	Ethyl cellosolve	7.9	4.5	7.0	11.5	PSA
32.	Ethylene glycol	8.3	5.4	12.7	16.1	NS
33.	Formamide	8.4	12.8	9.3	17.9	PSA
34.	Formic acid	7.0	5.8	8.1	12.2	PSA
35.	Glycerol	8.5	5.9	14.3	17.6	NS
36.	Hexamethyl phosphoramide ^b	9.0	4.2	5.5	11.3	S
37.	Methanol	7.4	6.0	10.9	14.5	NS
38.	Methyl acetate	7.6	3.5	3.7	9.1	NS
39.	Methyl cellosolve	7.9	4.5	8.0	12.1	PSA
40.	Methyl ethyl ketone	7.8	4.4	2.5	9.3	PSA
41.	4-Methyl-2-pentanol	7.6	4.3	6.5	10.9	NS
42.	<i>N</i> -methyl-2-pyrrolidone	8.8	6.0	3.5	11.2	S
43.	Methylene chloride	8.9	3.1	3.0	9.9	GSA
44.	Nitrobenzene	9.8	4.2	2.0	10.9	GSA
45.	Nitroethane	7.8	7.6	2.2	11.1	GSA
46.	Nitromethane	7.7	9.2	2.5	12.0	GSA
47.	1-Propanol	7.8	3.3	8.5	12.0	NS
48.	Propylene carbonate	9.8	8.8	2.0	13.3	GSA
49.	Propylene glycol	8.2	4.6	11.4	14.8	NS
50.	Pyridine	9.3	4.3	2.9	10.7	GSA
51.	2-Pyrrolidone	9.5	8.5	5.5	13.9	GSA
52.	Styrene	9.1	0.5	2.0	9.3	NS

TABLE I (Continued from the previous page.)

No.	Liquid	$\delta_{d,P}$	$\delta_{p,P}$	$\delta_{h,P}$	$\delta_{t,P}$	Extent of solubility
53.	Tetrahydrofuran	8.2	2.8	3.9	9.5	GSA
54.	Tetralin	9.6	1.0	1.4	9.8	PSA
55.	Tetramethylurea	8.2	4.0	5.4	10.6	S
56.	1,1,1-Trichloroethane	8.3	2.1	1.0	8.7	NS
57.	Triethyl phosphate	8.2	5.6	4.5	10.9	PSA
58.	Trimethyl phosphate	8.2	7.8	5.0	12.4	GSA
59.	Toluene	8.8	0.7	1.0	9.1	NS

^a S: solvent, GSA: good swelling agent, PSA: poor swelling agent, NS: nonsolvent.

^b Besides continuously shaken at 25°C for 7 days, this sample was heated at 100°C and kept at the temperature for 24 h.

Our X-ray analysis did show that OSPI had some crystallinity. Nevertheless, the crystallinity of OSPI did not affect our solubility experiments significantly under our experimental condition (at 100°C for 24 h).

Solubility Parameters from Solubility Experiments

The solubility region of OSPI in the three-dimensional Hansen space as well as the total solubility parameter, composed of dispersion ($\delta_{d,P}$), polar ($\delta_{p,P}$), and hydrogen bonding ($\delta_{h,P}$) forces have been determined as follows. Each liquid used for solubility experiments have been represented as a point on a three-dimensional plot with δ_d , δ_p , and δ_h as axes. For each axis a region with limits corresponding to the minimum and maximum values of the three components for both the solvents and good swelling agents have been first considered and divided into 10 equal parts.

The boundary of the solubility region for each of the 10 δ_d - δ_p , δ_d - δ_h , and δ_p - δ_h planes have been drawn in such a way to include all the solvents and exclude all the nonsolvents as well as poor swelling agents, with good swelling agents at the boundary. The analytical representation of the solubility region in the three-dimensional Hansen space is obtained by a computer iteration based on the least-square method. A two- and three-dimensional solubility plot of the OSPI in terms of Hansen parameters are shown in Figure 2, viewed from the point (20, 20, 20). The solubility region in the Hansen space is represented by a spheroid, best fitted by eq. (2).

$$(\delta_d - \delta_{d,P})^2 + (\delta_p - \delta_{p,P})^2 + (\delta_h - \delta_{h,P})^2 = 5.49^2 \quad (2)$$

where the parameters with subscript P referred to the center of spheroid coordinates corresponding to the solubility parameter of OSPI. The following values of the three-dimensional parameters of OSPI have been evaluated: $\delta_{d,P} = 10.6 \text{ cal}^{1/2}/\text{cm}^{3/2}$, $\delta_{p,P} = 5.3 \text{ cal}^{1/2}/\text{cm}^{3/2}$, and $\delta_{h,P} = 5.3 \text{ cal}^{1/2}/\text{cm}^{3/2}$ according to eq. (2).⁸⁻¹⁰ The total solubility parameter $\delta_{t,P}$ is $12.96 \text{ cal}^{1/2}/\text{cm}^{3/2}$ after calculation according to eq. (3).

$$\delta_{t,P}^2 = \delta_{d,P}^2 + \delta_{p,P}^2 + \delta_{h,P}^2 \quad (3)$$

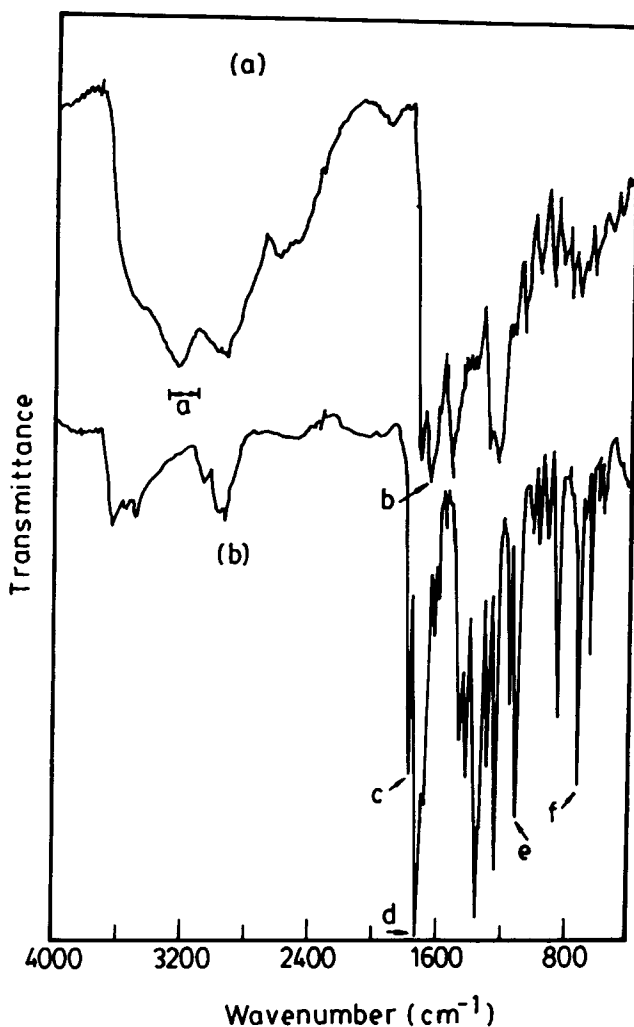


Fig. 1. The infrared spectra of polyamic acid and OSPI. (a) Polyamic acid; (b) OSPI. a: 3100–3300 cm^{-1} ; b: 1660 cm^{-1} ; (c): 1780 cm^{-1} ; d: 1730 cm^{-1} ; e: 1100 cm^{-1} ; f: 720 cm^{-1} .

The majority of the solvents are within the spheroid, and others are out of the spheroid. However, there are still two exceptional liquids: *m*-cresol, which is out of solubility region but can dissolve the OSPI, and triethyl phosphate, which is within the spheroid and cannot dissolve the OSPI.

Total Solubility Parameter from Equilibrium Swelling Method

The equilibrium swelling ratios of OSPI films in various mixture solvents at 25°C are shown in Tables II and III, which also list the solvents' solubility parameters calculated from eq. (4).

$$\delta = \sum_i i_{\phi} i_{\delta} \quad (4)$$

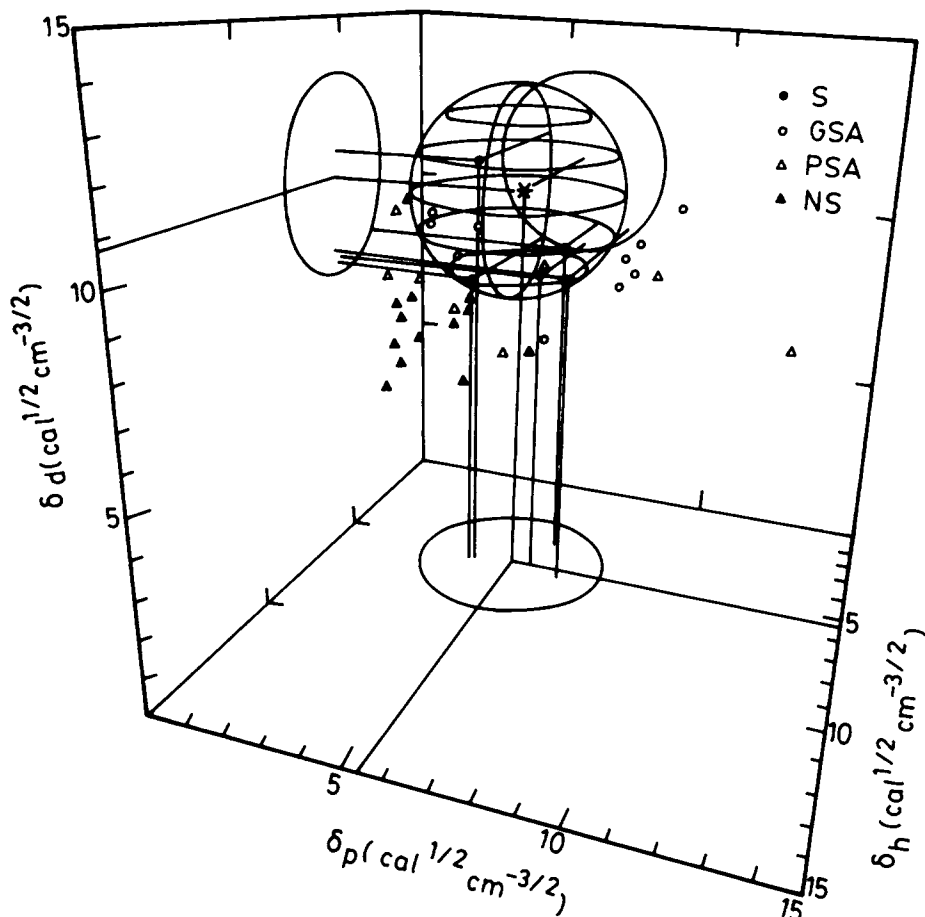


Fig. 2. Solubility region of OSPI in the Hansen space.

where j_ϕ is the volume fraction of i species and i_δ is the solubility parameter of i species. The highest equilibrium swelling ratios are reached in 10% v/v water in acetonitrile and 7%, v/v water in methyl cellosolve, which correspond to total solubility parameter of 13.1 and 12.9 $\text{cal}^{1/2}/\text{cm}^{3/2}$, respectively. From these results, it follows that the $\delta_{t,P}$ value is between 12.9 and 13.1 $\text{cal}^{1/2}/\text{cm}^{3/2}$.

Theoretical Calculations of the Solubility Parameters of OSPI

Alternative theoretical and semiempirical methods could be used to evaluate the polymer solubility parameter as well. Among them, the group contribution theory was widely used. Based on an examination of a vast amount of data on simple liquids, Fedors²¹ found that a general system for estimating both energy of vaporization ΔE_v and molar volume V could be set up simply by assuming eqs. (5) and (6).

$$\Delta E_v = \sum_i \Delta e_i \quad (5)$$

$$V = \sum_i \Delta v_i \quad (6)$$

TABLE II
Equilibrium Swelling Ratios of OSPI Films in Mixtures of Acetonitrile and Water

Solvent (v/v)	Equilibrium swelling ratio (%)	Solubility parameter δ (cal ^{1/2} /cm ^{3/2})
3% water + 97% acetonitrile	16.1	12.3
6% water + 94% acetonitrile	20.5	12.6
8% water + 92% acetonitrile	23.2	12.8
9% water + 91% acetonitrile	23.8	13.0
10% water + 90% acetonitrile	27.5	13.1
11% water + 89% acetonitrile	24.7	13.2
12% water + 88% acetonitrile	22.7	13.3
13% water + 87% acetonitrile	20.5	13.4
15% water + 85% acetonitrile	14.8	13.6

where Δe_i is additive atomic and group contribution for the energy of vaporization and Δv_i is additive atomic and group contribution for the molar volume. For high molecular weight polymers that have a T_g greater than 25°C, this divergence in the V values can be taken into account by the interaction of small correction factors, namely,

$$\Delta v_i = 4n \quad \text{for } n < 3$$

$$\Delta v_i = 2n \quad \text{for } n \geq 3$$

where n is the number of main chain skeletal atoms in the smallest repeating unit of the polymer. This includes all the skeletal atoms in a ring that may be part of the main chain. Using eqs. (5) and (6), the solubility parameter of high molecular weight polymer becomes

$$\delta = \left(\frac{\sum_i \Delta e_{ir}}{\sum_i \Delta v_{ir}} \right)^{1/2} \quad (7)$$

TABLE III
Equilibrium Swelling Ratios of OSPI Films in Mixtures of Methyl Cellosolve and Water

Solvent (v/v)	Equilibrium swelling ratio (%)	Solubility parameter δ (cal ^{1/2} /cm ^{3/2})
5% water + 95% methyl cellosolve	9.3	12.7
6% water + 94% methyl cellosolve	9.5	12.8
7% water + 93% methyl cellosolve	24.7	12.9
8% water + 92% methyl cellosolve	14.9	13.0
9% water + 91% methyl cellosolve	9.0	13.1
10% water + 90% methyl cellosolve	6.8	13.2

where Δe_{ir} is additive atomic and group contribution of the repeating unit for the energy of vaporization and Δv_{ir} is additive atomic and group contribution of the repeating unit for the molar volume. The group contribution of Δe_{ir} and Δv_{ir} taken from the literature²¹ is shown in Table IV. The evaluating process is as follows:

	Δe_{ir}	Δv_{ir}
1 phenyl (hexasubstituted)	7630	-23.6
2 phenyl (trisubstituted)	$2 \times 7630 = 15260$	$2 \times 33.4 = 66.8$
5 C=O	$5 \times 4150 = 20750$	$5 \times 10.8 = 54.0$
2 N	$2 \times 1000 = 2000$	$2(-9.0) = -18.0$
5 (5 or 6 member rings)	$5 \times 250 = 1250$	$5 \times 16 = 80$
Skeletal atoms		$2 \times 29 = 58$
	51390	351.2

Then, the total solubility parameter is evaluated according to eq. (7).

$$\delta = \left(\frac{\sum_i \Delta e_{ir}}{\sum_i \Delta v_{ir}} \right)^{1/2} = \left(\frac{51390}{351.2} \right)^{1/2} = 12.1 \text{ cal}^{1/2}/\text{cm}^{3/2}$$

Koenhen and Smolders²⁸ correlated solubility parameters of various solvents with physical properties such as surface tension, dipole moment, and refractive index with regard to the evaluation of the polymer dispersion parameter. They proposed

$$\delta_{d,P} = 9.55n_D - 5.55 \quad (8)$$

where n_D was the refractive index of the polymer. Because refractive index of OSPI is 1.687, $\delta_{d,P}$ is 10.56 cal^{1/2}/cm^{3/2} after calculation. Though n_D of various solvents under investigation were between 1.3 and 1.6, the $\delta_{d,P}$ of OSPI obtained from eq. (8) and from solubility experiments are consistent.

The experimental and calculated solubility parameters are collected in Table

TABLE IV
Group Contribution to Energy of Vaporization Δe_{ir} and Molar Volume Δv_{ir} ^a

Group	Δe_{ir} (cal/mol)	Δv_{ir} (cm ³ /mol)
CH ₃	1125	33.5
Phenyl (trisubstituted)	7630	33.4
Phenyl (hexasubstituted)	7630	-23.6
Ring closure 5 or 6 atoms	250	16
C=O	4150	10.8
N	1000	-9.0

^a From Fedors.²¹

TABLE V
Comparison of Experimental and Calculated Solubility Parameters ($\text{cal}^{1/2}/\text{cm}^{3/2}$) of OSPI

Method	$\delta_{d,P}$	$\delta_{p,P}$	$\delta_{h,P}$	$\delta_{t,P}$
Solubility experiments	10.6	5.3	5.3	12.96
Group contribution ^a	—	—	—	12.1
Refractive index	10.56	—	—	—
Equilibrium swelling method	—	—	—	12.9–13.1

^a Calculated from Fedors method.

V. All the results are in very good agreement except that the result obtained from the Fedors method appears to be low in comparison with the experimental results.

CONCLUSION

Solubility experiments and equilibrium swelling methods have been carried out to evaluate the solubility parameters of organic soluble polyimide (OSPI). The solubility behavior of OSPI has been examined in about 60 liquids. We found that only six liquids are capable of dissolving OSPI. From the Hansen space, we calculate that the total solubility parameter of OSPI is $12.96 \text{ cal}^{1/2}/\text{cm}^{3/2}$ and its components are $\delta_{d,P} = 10.6 \text{ cal}^{1/2}/\text{cm}^{3/2}$, $\delta_{p,P} = 5.3 \text{ cal}^{1/2}/\text{cm}^{3/2}$, and $\delta_{h,P} = 5.3 \text{ cal}^{1/2}/\text{cm}^{3/2}$, respectively. The total solubility parameter measured from equilibrium swelling methods is between $12.9 \text{ cal}^{1/2}/\text{cm}^{3/2}$ and $13.1 \text{ cal}^{1/2}/\text{cm}^{3/2}$, which is in good agreement with the result obtained from solubility experiments. The dispersion contribution parameter calculated from the correlation of $\delta_{d,P}$ with refractive index of OSPI is $10.56 \text{ cal}^{1/2}/\text{cm}^{3/2}$ and is also close to the result from solubility experiments. The theoretical value of total solubility parameter calculated from the Fedors method shows some deviations from others, and the discrepancy between the calculated and experimental result is approximately 6.6%.

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Received April 18, 1989

Accepted June 8, 1989