

The Solubility Parameters of Aromatic Polyamides

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SYNOPSIS

The degrees of swelling of rigid aromatic polyamide networks in various solvents, nonsolvents, and solvent mixtures were used to determine their solubility parameters. This was made possible because of the amorphous nature of the rigid networks and the low levels of intersegmental H-bonding. The solubility parameters are: $\delta = 23.0 \text{ (MPa)}^{1/2}$, $\delta_d = 18.0 \text{ (MPa)}^{1/2}$, $\delta_p = 11.9 \text{ (MPa)}^{1/2}$, and $\delta_H = 7.9 \text{ (MPa)}^{1/2}$. The determined values are believed to be good approximations of the solubility parameters of stiff linear aromatic polyamides, because of the essential identity of their structure and the stiff segments in the networks.

INTRODUCTION

It has been shown by Hansen¹ that the solubility parameter δ can be divided into three parts

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_H^2 \quad (1)$$

where δ_d represents the part of δ due to dispersion forces, δ_p is the part due to dipolar forces, and δ_H is the contribution of hydrogen bonding (H-bonds) effects and other donor-acceptor interactions. To the best of our knowledge, there exists in the literature only one δ value of the aromatic linear polyamide poly(*p*-phenylene terephthalamide), calculated by group additivity procedures.² Identical values of δ_d and δ_H for two aromatic copolyamides poly(*m*-phenylene tere-co-isophthalamide) were calculated by Matsuura et al.³ from liquid chromatographic results.

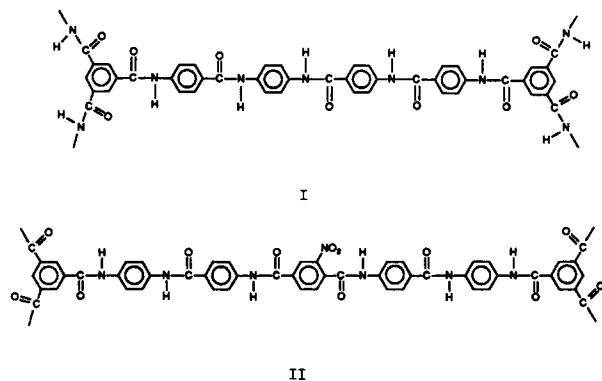
We believe that the absence of experimental δ values for linear aromatic polyamides, such as poly(*p*-benzamide), poly(*p*-phenylene terephthalamide), and poly(*p*-benzanilide terephthalamide), is due to the extremely high concentration of interchain H-bonds in these systems. This high concentration is largely due to the fact that these stiff linear polyamides prefer to align themselves in parallel arrays, maximizing the accessibility of amide groups to interchain H-bond formation, and that the amide

groups are spaced along the chains at about even distances, such that the formation of one interchain H-bond greatly facilitates the formation of all possible additional H-bonds between the two interacting chains. The tendency toward parallel alignment leads to high anisotropic packing and crystallinity in the solid state, to liquid crystalline behavior in concentrated solutions,⁴ and to molecular aggregation, detectable by light scattering techniques, in the dilute solution regime.⁵ The point is that in the case of linear aromatic polyamides, very strong solvents are needed in order to break the profusion of interchain H-bonds. The most common solvents used for this purpose are concentrated H_2SO_4 and solutions of LiCl in N,N-dimethylacetamide (DMAc/LiCl). From these, concentrated sulfuric acid is the better solvent because it dissolves the aromatic polyamides at room temperature and it is less tolerant to interchain H-bonds. The solvent mixture DMAc/LiCl is not as potent, often requires some heating in order to dissolve the linear stiff polyamides, occasionally fails to dissolve them after they have been fully dried at elevated temperatures, and may leave behind microscopic gels and molecular aggregates.^{4,5}

EXPERIMENTAL

Recently, we prepared many families of networks and gels of highly branched, stiff aromatic poly-

amides.⁶⁻¹⁰ The networks are characterized by short stiff segments consisting of parasubstituted aromatic rings, crosslinked, in most instances, by rigid aromatic polyfunctional branchpoints at both ends. The connections between aromatic rings are exclusively by amide groups. Typical segments with their branchpoints are shown below:



In the gel state, the swollen networks were amorphous.^{7,8,9} When fully dried and collapsed, most networks retained their amorphicity.^{7,8,9} A few of them, with the longest straight segments between branchpoints, developed very small levels of crystallinity upon drying up and collapsing. Infrared spectroscopy showed that these also had the highest concentration of H-bonds.¹¹ The H-bond concentration in the dry networks sharply dropped off as the average length of the stiff segments decreased.¹¹ The amorphicity and sharply reduced number of H-bonds in the dry rigid networks reflect the random orientation of the individual stiff segments in the system and their inability correctly to position themselves such that interchain H-bonds will form. When placed in a good solvent, preferably with some heating, the networks, as well as their pre-gel highly branched rigid fractal polymer progenies, imbibed large volumes of the solvent and swelled. The properties and swelling behavior of the rigid aromatic polyamide networks and gels led to the conclusion that the solubility parameter, δ , of these networks can be determined and from it the solubility parameter of their linear, soluble analogues may be accurately estimated.

In this work, three series of swelling experiments were performed. In the first, 7 different networks were first swelled in neat DMAc and, after equilibration, were transferred to and equilibrated in two series of DMAc/methanol and DMAc/acetone mixtures. The volume changes were evaluated from both dimensional measurements and weighing of the gel slabs. Detailed descriptions of the swelling-deswelling equilibration procedures were previously

reported.⁶⁻⁹ In a second set of experiments, a variety of liquids were tested for the swelling ability of our networks. The liquids were selected in order to gain understanding of the significance of δ alone, δ_p alone, and δ_H . They are listed with their δ , δ_d , δ_p , and δ_H values in Table I. The third series of swelling experiments used 3 good solvents, and 3 1 : 1 vol/vol mixtures of these solvents, in order to obtain a good estimate of the values of δ , δ_d , δ_p , and δ_H for the networks and linear rigid aromatic polyamides. In the second and third series of experiments, the networks in the immersion liquids were heated for not more than 30 min at the lower of the liquid boiling temperatures, or 150°C, then cooled and allowed to rest at room temperature for at least 24 h prior to measurement.

The results of swelling of 7 rigid networks in DMAc, and their deswelling upon equilibration in DMAc/methanol and DMAc/acetone, are plotted in Figure 1 against the δ values of the neat liquids and their mixtures. They are all normalized such that the swelling in DMAc is set at 100%. It is important to mention here that the swelling in neat DMAc and in DMAc/5% LiCl were found to be identical^{7,8} for networks with Type I and Type II segments. This means that our networks did not benefit from the presence of LiCl in the system, probably because of the low concentration of interchain H-bonds initially present in the system. It is also of interest to note that when the gels deswelled, even in 100% nonsolvent, they retained a volume far larger than the volume of the polymer network alone. Similar results were previously observed in formamide.⁸ From Figure 1, we gather that for rigid aromatic polyamide networks, δ is expected to fall in the interval $21.5 \leq \delta \leq 23.5$ (MPa)^{1/2}. A test of the four liquids, DMAc, propionitrile, sec-butanol, and nitrobenzene, with $\delta = 22.7, 21.7, 22.1,$ and 22.1 (MPa)^{1/2}, respectively, indicated that of these only DMAc is a good swelling solvent for the networks. Therefore, the magnitude of δ is insufficient by itself to control the swelling or dissolution of rigid aromatic polyamides.

In the second experiment, the liquids from Table I were used in order to swell samples from the same rigid network, identified as 45 XD and characterized in Ref. 9. The ordinal numbers of the liquids in Table I are used to identify them in Figure 2. In Figure 2, solvents Nos. 1, 2, and 3 are inscribed in a region of the highest swelling. In it, the + symbol marks the location of δ and δ_p of our polymers, as calculated according to Koenhen and Smolders.¹³ The X symbol marks the location of δ and δ_p for our polymers, as per our estimate: δ from the center of the swelling peak in Figure 1 and δ_p by averaging the δ_p of the

Table I Liquids Used to Estimate the Solubility Parameters of Rigid Aromatic Polyamides¹²

No.	Name	Solubility Parameter in (MPa) ^{1/2}			
		δ_d	δ_p	δ_H	δ
1	N-Methyl-2-pyrrolidinone (NMP)	18.0	12.3	7.2	22.9
2	N,N-Dimethylacetamide (DMAc)	16.8	11.5	10.2	22.7
3	N,N-Dimethylformamide (DMF)	17.4	13.7	11.3	24.8
4	2-Pyrrolidone	19.4	17.4	11.3	28.4
5	Dimethylsulfoxide (DMSO)	18.4	16.4	10.2	26.6
6	Formamide	17.2	26.2	19.0	36.6
7	Acetone	15.5	10.4	7.0	20.1
8	Methyl isobutyl ketone (MIBK)	15.3	6.1	4.1	17.0
9	Methanol	15.1	12.3	22.3	29.7
10	Ethanol	15.8	8.8	19.4	26.6
11	Sec-Butanol	15.8	5.7	14.5	22.1
12	Glycerol	17.4	12.1	29.3	36.2
13	Pyridine	19.0	8.8	5.9	21.7
14	Propionitrile	15.3	14.3	5.5	21.7
15	Nitrobenzene	20.1	8.6	4.1	22.1
16	Tetrahydrofuran (THF)	16.8	5.7	8.0	19.4
17	Chloroform	17.8	3.1	5.7	19.0
18	Formic acid	14.3	11.9	16.6	25.0
19	Water	15.5	16.0	42.4	47.9

two best solvents, NMP and DMAc. The proximity of the X to NMP and DMAc reflects the fact that networks with segments Type II swell in them in room temperature and networks with Type I segments swell upon heating, both in the absence of LiCl. In DMF under identical conditions they swell only marginally.¹⁴

A larger region in Figure 2 covers modest swelling. In this area are included some of the DMAc/methanol and DMAc/acetone mixtures on the shoulders of the swelling peak in Figure 1, and the neat liquids 2-pyrrolidone and dimethylsulfoxide. All other liquids are nonswelling. The region of good swelling liquids is a relatively small one, spanning δ from 22.7 to 24.8 (MPa)^{1/2} and δ_p from 11.5 to 13.7 (MPa)^{1/2}. The two modest swelling liquids (Nos. 4 and 5) have too high δ and δ_p values, but the values of their δ_d and δ_H are close to those of the good swelling agents.

The third set of experiments was conducted in order to improve our estimate of δ and δ_p . The same network was used as for the second series (45 XD). The solvent retention upon swelling of the comminuted network is indicated in arbitrary units (solvent weight) for each solvent and solvent mixture in Figure 3. From Figure 3 we learn that the solvent quality goes as: NMP > DMAc > DMF and that for the mixtures, 1 : 1 NMP/DMAc > 1 : 1 NMP/DMF

> 1 : 1 DMAc/DMF. The position of the X in Figure 3 reflects the swelling power of the solvents and their mixtures, and takes cognizance of the value of δ as obtained in Figure 1.

The values of δ and δ_p for our polyamides, calculated according to Koenhen and Smolders,¹³ are substantially out of the triangle inscribed by the solvents NMP, DMAc, and DMF. The values of $\delta = 29$ (MPa)^{1/2}, calculated by Iyengar² from group additivity,¹⁵ and $31.3 < \delta < 32.9$ (MPa)^{1/2}, calculated by Rutledge and Suter¹⁶ from multichain energy minimization, are far from all our results. Therefore, all these values appear to us to be unacceptable. In the work of Matsuura et al.,³ the density of the aromatic polyamide was assumed to be 1.2 g/cm³. This is lower than the value of 1.277 g/cm³ determined in our laboratory on our dry network by high pressure mercury porosimetry.⁹ Also, Matsuura et al.³ appear to have lumped both δ_p and δ_H together under a single value, which, by itself, is too high to be either δ_p or δ_H alone.

From the swelling studies, we elected the value of $\delta = 23$ (MPa)^{1/2} as the best estimate for δ of rigid aromatic polyamide networks. The value of $\delta_d = 18.0$ (MPa)^{1/2} is an average between $\delta_d = 18.3$ (MPa)^{1/2}, obtained by Matsuura et al.,³ and $\delta_d = 17.7$ (MPa)^{1/2}, calculated by us for the rigid polyamides according to Koenhen and Smolders.¹³ The value of $\delta_p = 11.9$

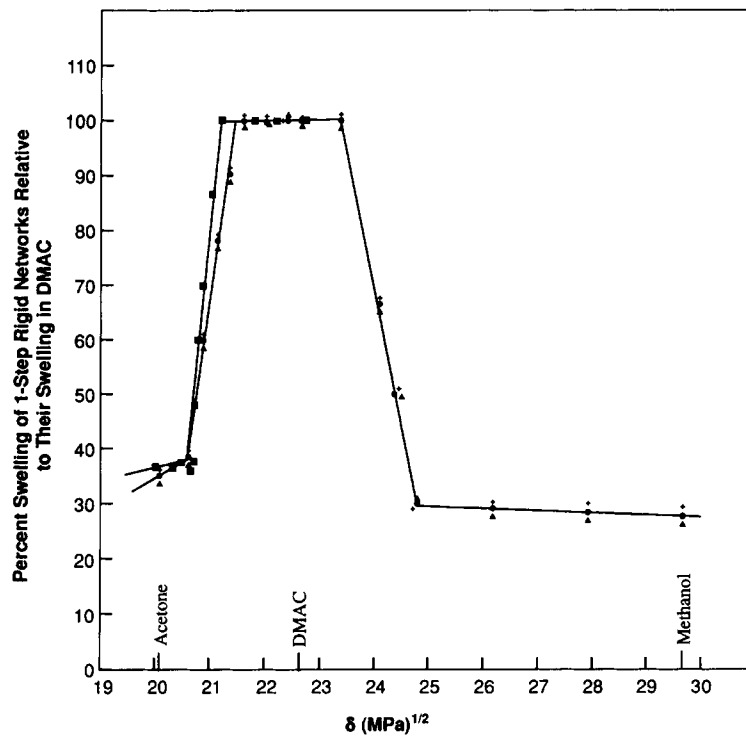


Figure 1 Normalized swelling of rigid polyamide networks in DMAC/methanol and DMAC/acetone relative to their swelling in DMAC.

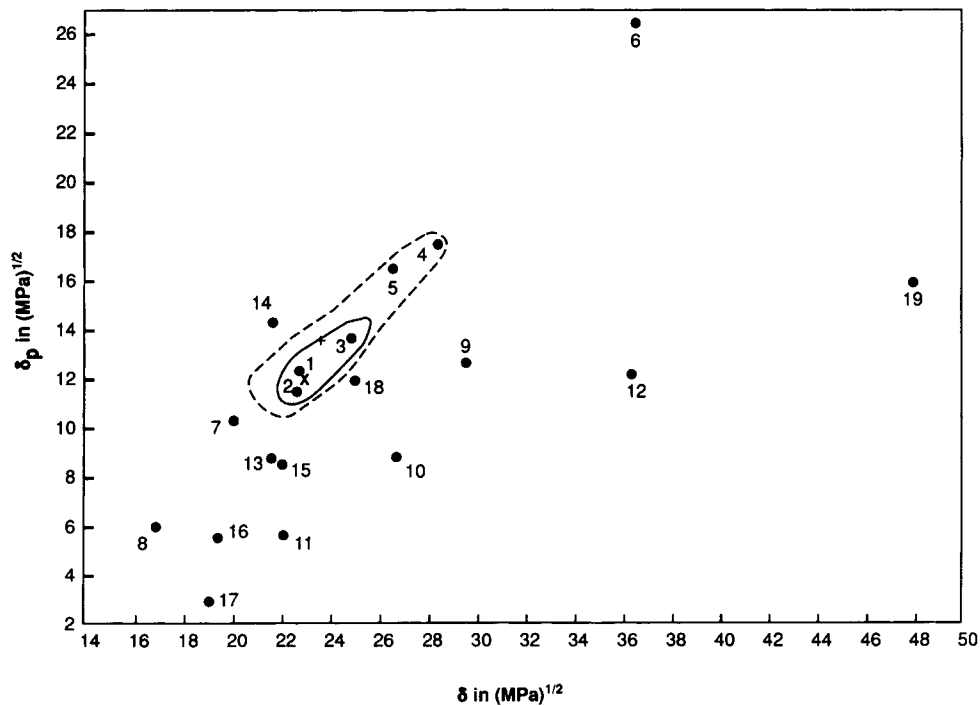


Figure 2 Swelling map of rigid polyamide network, plotted on a grid of the δ and δ_p values of the tested swelling liquids. Additional explanations in text.

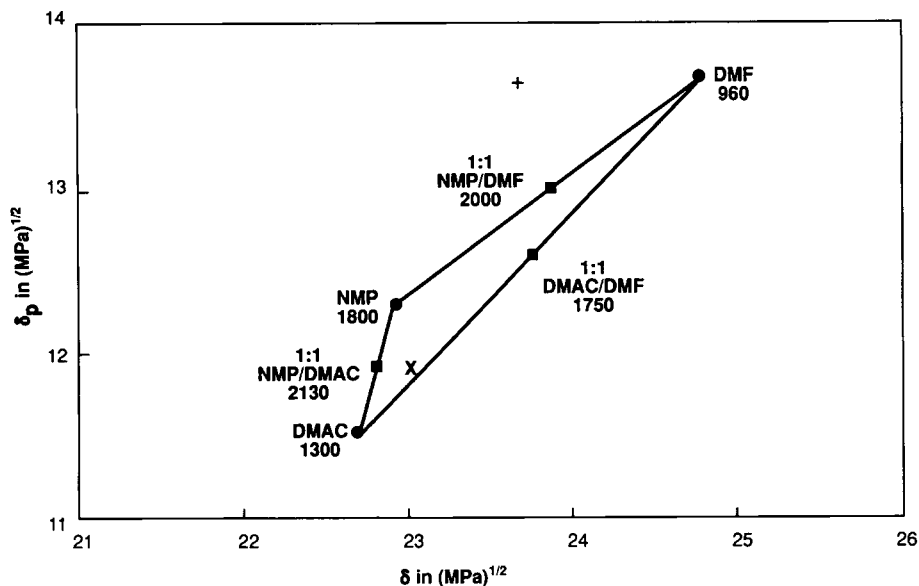


Figure 3 Swelling map of rigid polyamide network, plotted on a grid of the δ and δ_p values of NMP, DMAc, DMF, and their 1 : 1 vol/vol mixtures. (+) Solubility parameters for the network calculated according Koenhen and Smolders.¹³ (X) Solubility parameters of the same network as per our estimate.

(MPa)^{1/2} is identical with that of 1 : 1 NMP/DMAc, which produced the largest swelling of the aromatic polyamide network, shown in Figure 3. By the use of eq. (1), we are led to $\delta_H = 7.9$ (MPa)^{1/2}, which is slightly higher than the 7.7 (MPa)^{1/2} calculated according to Ref. 13, and the $\delta_H = 7.2$ (MPa)^{1/2} of NMP. We conclude, hence, that a best estimate of δ for rigid aromatic polyamide networks containing an occasional nitro group is: $\delta = 23.0$, $\delta_d = 18.0$, $\delta_p = 11.9$, and $\delta_H = 7.9$ (MPa)^{1/2}. Because of the similarity in behavior, these values are expected to be good approximations for unnitrated rigid polyamide networks; because of the compositional similarity between the networks and their soluble linear aromatic polyamides, the above solubility parameter values are valid for these polymers too.

Finally, the relationships

$$\delta^2 = e_{\text{coh}} \quad (2)$$

and

$$\gamma \cong 0.75e_{\text{coh}}^{2/3} \quad (3)$$

may be used to estimate the surface tension, γ , of the polyamides from their cohesive energy density, e_{coh} .¹⁵ From $\delta = 23.0$ (MPa)^{1/2}, a value of $\gamma = 49.0$ mN/m (=dyn/cm) is obtained. This is close to $\gamma = 48.5$ mN/m obtained in adhesion tests of unsized poly(p-phenylene terephthalamide) fibers.¹⁷

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