New Sets of Solubility Parameters of Linear and Crosslinked Aromatic Polyamides

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ABSTRACT: As generally accepted, also in the case of polyamides linear and crosslinked polymeric materials are believed to be characterized by the same solution properties and, consequently, by the same solubility parameters. However, despite their great practical importance, a thorough study aimed to determine the best solvent media able to dissolve linear aromatic polyamides has not been performed yet or, at least, has not been published. In this study, we report on our study on the solubility parameters of linear and crosslinked aromatic polyamides. We demonstrate that the assumption of considering these two classes as having the same solubility properties can lead to dramatically erroneous results. Two new different sets for linear and crosslinked aromatic polyamides are proposed. Namely, linear poly(p-phenylene terephthalamide) is characterized by δ_p, δ_d, and δ_H equal to 8.6, 18.4, and 11.3, respectively; by contrast, the corresponding values of the crosslinked aromatic polyamides taken into consideration are: 11.5, 16.8, and 10.2.© 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 3155–3160, 2010

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INTRODUCTION

Poly(p-phenylene terephthalamide) (PPDT) is the leading term of the class of aromatic polyamides. Because of its outstanding mechanical and flame resistance properties, the whole para-orientation, joined to the absence of substituents, confers a high rigidity to PPDT linear chains and allows for strong interactions mainly due to H-bonding. These two factors are responsible for many features of PPDT, namely, its high crystallinity, the lyotropic behavior and the very difficult dissolution in organic solvents. On this respect, it is useful to remind that the only solvents of PPDT able to molecularly dissolve it are concentrated sulfuric acid and mixtures of hexamethyl phosphoric triamide (HMPA) with either *N*-methyl pyrrolidone (NMP) or dimethyl acetamide (DMAc), in the presence of LiCl and/or CaCl$_2$.[1] The latter mixtures were initially used as solvents for both the PPDT synthesis and the spinning of its fibers (Kevlar®, Twaron®); however, when HMPA was recognized as a very toxic carcinogenic chemical, its use in industrial applications was abandoned.

Subsequently, alternative solvents, such as, NMP or DMAc with some amounts of the aforementioned inorganic salts, have been used. It is believed that the increased solubility found in the presence of salts is due to their ability of complexing the amide groups.[1]

In any case, during its synthesis the above systems are not able to keep high MW PPDT in a real molecular solution, but only in a quasi gel state. This drawback limits the possibility of reaching very high degree of polymerization, actually obtained only in HMPA/NMP/LiCl solution. In particular, NMP/CaCl$_2$ mixtures are those commonly used in the industrial PPDT preparation.[1]

In our opinion, a thorough study on the solubility characteristics of PPDT, namely, the evaluation of its solubility parameters, is necessary in order to find out the most suitable solvents to replace HMPA, still compatible with the reactants used in the PPDT synthesis. Surprisingly, to our knowledge such study has not been reported in the open literature so far. The only experimental works related to this topic is due to Aharoni[2] who evaluated the solubility parameters of some crosslinked aramids (CAs), characterized by short, stiff segments consisting of p-substituted aromatic rings (A-I and A-II in Fig. 1). In these papers, Aharoni claims that CAs solubility parameters can be used for linear aramids as well and, in particular, for PPDT itself.

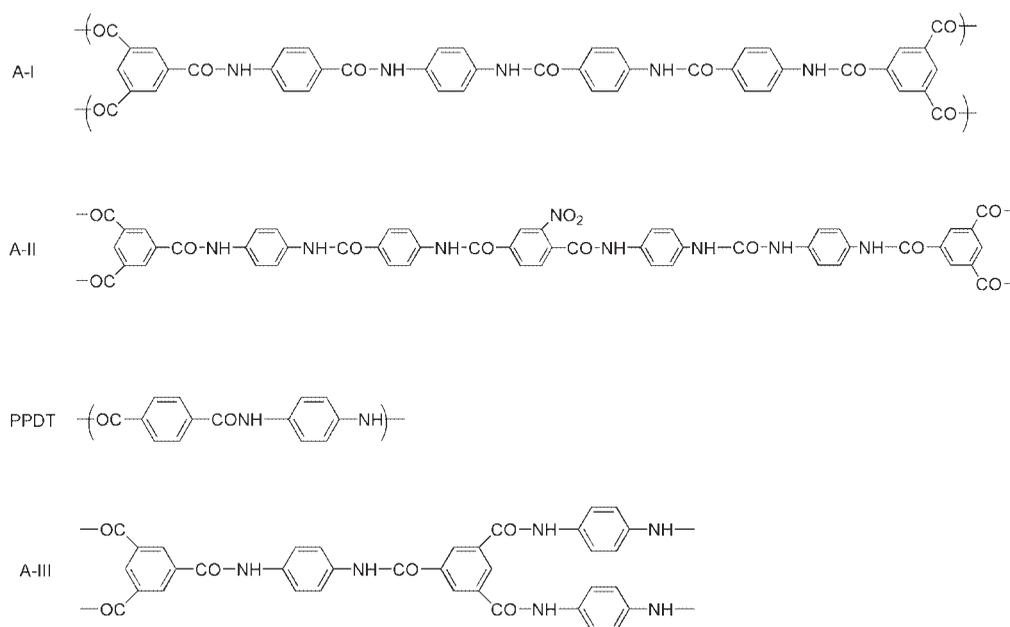*Correspondence to:* A. Mariani (mariani@uniss.it).

Figure 1 Aromatic polyamides considered in this work: (a) A-I, A-II: Aromatic polyamides studied in Ref. 2; (b) PPDT, A-III: Aromatic polyamides studied in this work.

As suggested by Hansen,[3] the solubility parameter δ comes from three contributions, as follows:

$$\delta^2 = \delta_d{}^2 + \delta_p{}^2 + \delta_H{}^2$$

where δ_d, δ_p, and δ_H are the terms linked to dispersion, polar, and hydrogen bonding forces, respectively. It is well-known that, when a solvent is characterized by solubility parameters as close as possible to that of a specific polymer, the pair can give rise to a homogeneous solution.

Besides the theoretical calculation of $\delta_{polymer}$ by the group contribution method,[4] one of the most frequently used methods for experimentally determining the solubility parameters of a linear polymer is to evaluate the swelling behavior of the corresponding crosslinked structure.[2] As linear polymers are generally soluble in a large number of chemicals, it is not always possible a direct δ evaluation, and it is commonly accepted that the linear polymer and its crosslinked counterpart are characterized by the same solubility parameters.[4–7] However, great attention should be paid to structural analogies and differences between the two systems before making the above assumption. In our opinion, this can be the case for PPDT and the corresponding CAs synthesized so far, which are characterized by a dendritic fractal architecture.

Indeed, as reported in literature,[2] the network rigidity of CAs does not allow extensive H-bonding interactions among close segments. However, H-bonds are most likely the major responsible factors for the very limited solubility of PPDT. A word of caution is therefore needed.

An alternative route to δ evaluation from swelling measurement is, however, possible as, due to the insolubility of PPDT in neat organic solvents and their mixtures, its swelling behavior in the above media can be directly tested and compared with that of CAs, in order to experimentally check whether the two kinds of aramid structures are characterized by the same δ or not.

In this article, we report on our study devoted to the evaluation of PPDT swelling behavior versus that of some CAs in various solvents. New sets of δ, δ_d, δ_p, and δ_H values for the above polymers are proposed.

EXPERIMENTAL PART

All solvents used in this work were purchased by Aldrich and used as received. LiCl (Carlo Erba), LiClO$_4$, LiBr, (Aldrich), and CaCl$_2$ (Fluka) were dried for 24 h in an oven at 320°C under vacuum.

PPDT and CA samples, named here A-III and derived from the reaction between 1,3,5-benzenetricarboxylic acid and *p*-phenylenediamine (Fig. 1), were synthesized in our research group following the procedures already reported[8–13]; in the above references, our CA was named poly(A$_2$ + B$_3$).

The evaluation of the degree of swelling (Δ*V* %) was gravimetrically performed after proper polymer equilibration in the solvent medium (150°C or reflux for 30 min, 24 h at room temperature, 100°C or

TABLE I
Solvent Parameters (MPa$^{1/2}$) of the Neat Liquids Used in this work[5] and ΔV % of PPDT and A-III

Solvent	δ	δ_p	δ_d	δ_H	ΔV %	
					PPDT	A-III
NMP	22.9	12.3	18.0	7.2	276	3400
HMPA	23.3	8.6	18.4	11.3	544	100
Formic acid	25.0	11.9	14.3	16.6	199	–
1,2-Dibromoethane	23.9	6.8	19.6	12.1	48	–
DMSO	26.6	16.4	18.4	10.2	269	3200
Pyridine	21.7	8.8	19.0	5.9	236	–
DMF	24.8	13.7	17.4	11.3	249	3200
DMAc	22.7	11.5	16.8	10.2	287	4600
Acetone	20.1	10.4	15.5	7.0	97	–

reflux for 36 h followed by 48 h at room temperature).

RESULTS AND DISCUSSION

Salt-free solvent media

PPDT

The media used in this work for testing the PPDT swelling, together with the corresponding δ, δ_d, δ_p, and δ_H values, are listed in Table I.[5] As can be seen, a wide range of liquids have been selected for a thorough study on their action.

In the same table, the swelling behavior of our PPDT sample in the above solvents is given. As expected, liquids characterized by the same δ parameter give rise to widely different extents of swelling, thus confirming that the overall δ is not able to reveal and interpret the solubility behavior of a polymer in which polar forces and H-bonds are not at all negligible.

Indeed, HMPA has a δ value close to those of NMP, DMAc, and 1,2-dibromoethane, but the degree of PPDT swelling reached in its presence is much higher than those attained by the other solvents.

Furthermore, NMP, DMSO, pyridine, DMF, and DMAc give comparable ΔV %, although their δ values range from 21.7 to 26.6 MPa$^{1/2}$.

The same conclusion is also achieved by considering the specific δ_d, δ_p, and δ_H values.

However, in the light of the above findings, a selection of the best swelling media can be done, including: HMPA, NMP, DMAc, DMF, and DMSO.

In a second set of experiments, several binary mixtures of the above best solvents were prepared and the extent of swelling was determined as a function of the composition of each liquid. The best results for each solvent or solvent pair are summarized in Table II. As can be seen, neat HMPA gives the highest degree of swelling.

Moreover, the best two solvent mixtures recommended in literature (i.e., NMP/DMAc and NMP/ DMF),[2] although characterized by degrees of swelling higher than those of the corresponding neat solvents (ΔV % = 331 and 351, respectively), give worse results when compared with neat HMPA (540%).

On this basis, we can conclude that the solubility parameter of HMPA should be considered as the most accurate estimation for the determination of that of PPDT than the values previously suggested (Table III).

Crosslinked aramids

For comparison with what has been previously reported in literature,[2] the swelling behavior of our CA (A-III) has been tested in the following media: NMP, DMAc, DMF, DMSO, and HMPA. This latter solvent was not taken into account by Aharoni.[2]

Table I gives the degree of swelling of our CA in presence of the above media. Surprisingly, even if HMPA in binary mixtures with NMP represents the best medium based on organic solvents found so far for PPDT, in the case of A-III, it shows the poorest solvent properties. Moreover, with the notable exception of this latter solvent, all other media are able to swell our CA to a rather large extent. Namely, the following order for ΔV % has been found: DMAc > NMP > DMSO $\cong$ DMF >> HMPA.

TABLE II
Best Solvent Media Found for PPDT and A-III

Aramid	Solvent	Composition (v/v)	ΔV %
PPDT	DMSO/DMAc	8/1	311
	DMSO/NMP	1/1	322
	DMAc/NMP	1/1	331
	DMF/DMAc	6/1	341
	DMF/NMP	2/5	351
	HMPA	Neat	540
A-III	DMF/NMP	1/1	3790
	DMF/DMSO	1/1	3591

TABLE III
Solubility Parameters (MPa$^{1/2}$) of both Linear and
Crosslinked Aramids: Comparison with Literature Data

	δ	δ_d	δ_p	δ_H
Ref. 2	23.0	11.9	18.0	7.9
CAs (this work)	22.7	11.5	16.8	10.2
PPDT (this work)	23.3	8.6	18.4	11.3

We have also measured the degree of swelling in the presence of two binary mixtures based on DMF but, as shown in Table II, although it results to be about 11–15% higher than the average value of the neat components, it remains still much lower than that found for DMAc alone (4600%). The latter value is significantly larger than that reported in the literature[2] for the system DMAc/NMP in which the above pair was considered as the best solvent medium for CAs. Consequently, at least in the case of our CA, the solubility parameter and its specific contribution derived from neat DMAc[5] have been taken as a better approximation in comparison with those characterizing the previously considered CAs.[2] The new set of values is reported in Table III (second vs. first line).

A specific comment should be devoted to HMPA, which behaves as the best organic solvent for linear aromatic polyamides, but it is a rather poor solvent medium for CA (Table I). This fact should be considered as a strong evidence that linear and crosslinked structures (namely, those formed via intermediate hyperbranched structures as in the case of Aharoni's[2] and in this work) cannot be compared in a straightforward manner, not always having similar behaviors. In particular, in this case, the role played by the strong H-bonding interactions among the lin-
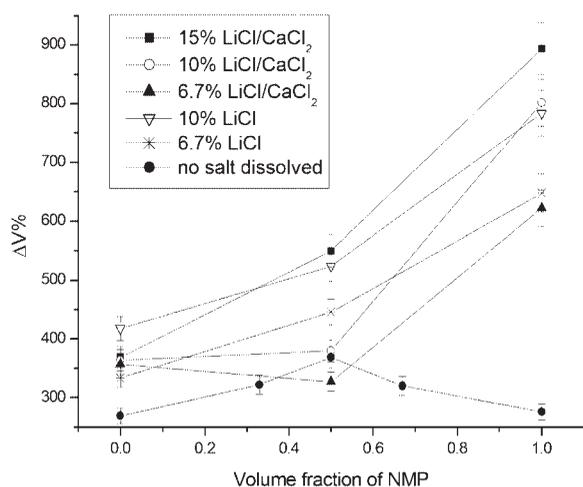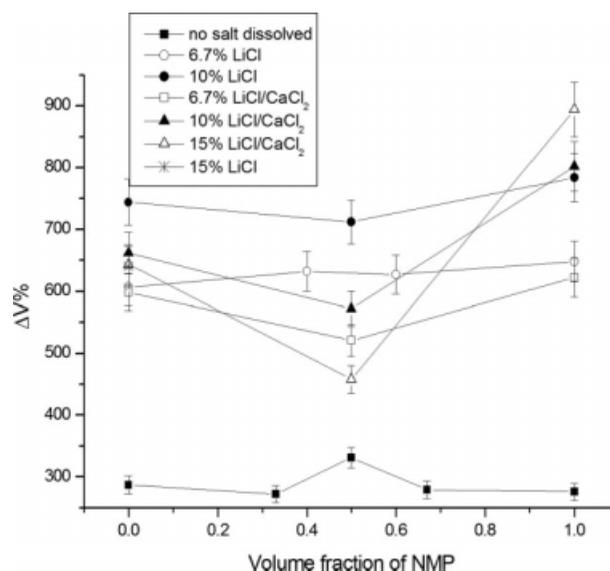

Figure 3 ΔV % of PPDT in various NMP/DMAc solvent mixtures and effect of the type and concentration of dissolved salt(s).

ear aramid chains is most likely completely different as compared with that of CAs, which is characterized by a peculiar crosslinked architecture. Moreover, the possibility of giving rise to ordered aggregates of oriented macromolecular chains is probably prevented in CAs, which are characterized by more disordered and inhomogeneous structures.

As a consequence of the above findings, in order to confirm the different behavior of linear and CAs, a further comparative study was done. Namely, the effect of the presence of LiCl and CaCl$_2$ in the above solvents was investigated.

Salt-containing solvent media

PPDT

This set of experiments was performed by dissolving different amounts of LiCl or LiCl/CaCl$_2$ (1/3 w/w) in the best solvents shown above (DMAc, DMF, NMP, DMSO, and HMPA) as well as in all of their binary mixtures. Namely, the total weight concentration of salt was varied from 6.7 to 15 wt %. This range was chosen in agreement with what is reported in literature, where 6.7 wt % was suggested for PPDT synthesis[8–13] and 15 wt % was reported for its spinning.[14]

It has been found that the binary mixtures containing HMPA, added with the above salts, can completely dissolve PPDT when the concentration of HMPA is ≥33% (in mixtures with NMP, DMF, and DMAc), and ≥50% (in mixture with DMSO). Conversely, all other mixtures can only swell PPDT. Namely, ΔV % of PPDT in various NMP-containing binary mixtures is reported in Figures 2–4. As can

Figure 2 ΔV % of PPDT in various NMP/DMSO solvent mixtures and effect of the type and concentration of dissolved salt(s).

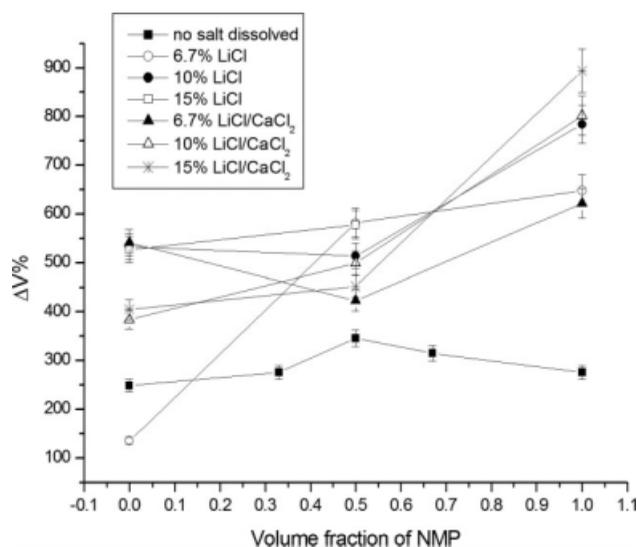**Figure 4** ΔV % of PPDT in various NMP/DMF solvent mixtures and effect of the type and concentration of dissolved salt(s).

be seen, all salt-containing binary mixtures of NMP with DMSO or DMF exhibit a poorer swelling capability than the corresponding NMP + salt(s) solvent media.

Conversely, although no large differences are found in the swelling behavior of the DMAc/NMP-based mixtures, neat NMP + 15 wt % LiCl/CaCl$_2$ shows the largest ΔV % ($\cong 900$).

To evaluate the role of the amount of dissolved salts, a study on the dependence of the degree of swelling on salt concentration has been done for NMP and DMAc (Fig. 5).

In both cases, the larger the amount of salts, the larger is ΔV %. Furthermore, no significant difference has been found by comparing mixtures contain-
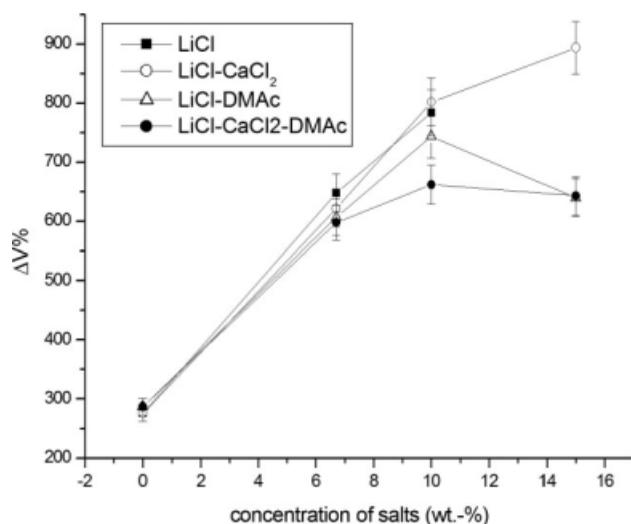

Figure 5 Effect of the salt type and concentration on the ΔV % of PPDT in DMAc.

TABLE IV
Dependence of CAs ΔV % on the Type of Lithium Salt in DMAc

Salt type	Salt concentration		ΔV %
	mol/L	wt %	
LiCl	0	0	4577
	0.1	0.42	2000
	1.5	6.76	720
LiBr	0.1	0.92	1550
LiClO$_4$	0.1	1.13	1400

ing equal total weight amount of LiCl + CaCl$_2$ with those containing LiCl only for any of the above solvents (Note: salt precipitation has been observed in NMP + 15% LiCl).

Crosslinked aramids

A set of experiments was carried out by adding 6.7 wt % of LiCl to the best solvents mentioned earlier. Such amount of salt was chosen equal to that used in the synthesis of PPDT according to what previously reported by us.[8–13]

ΔV % as a function of the amount of LiCl dissolved in DMAc is reported in Table IV. By considering the above table, it comes out that the presence of LiCl reduces the swelling capability of any liquid. Namely, as previously mentioned, although DMAc is the best CA solvent (ΔV % $\cong 4600$), even a relatively small amount of LiCl (0.42 wt %) causes sharp reduction of the swelling down to ΔV % $\cong 2000$.

To verify any possible effect of different anions, a comparison among LiCl, LiClO$_4$, and LiBr has been performed. As Table IV shows, all these salts reduce the capability of DMAc to swell CAs from 4577% to less than half-one-third, in the following order of Δ%: LiCl > LiBr > LiClO$_4$.

CONCLUSIONS

The swelling behaviors of crosslinked and linear aromatic polyamides have been investigated and a comparison between these macromolecular structures has been done. At variance to what is commonly reported in literature, it was found that such macromolecular architectures are not always characterized by the same solvent parameters. Indeed, the best solvent for linear PPDT has been found to be one of the worst for its crosslinked counterpart and vice versa, a different behavior probably due to the diverse contribution of hydrogen bonding and polar forces to polymer/polymer and polymer/solvent interactions. Besides, due to their much disordered structure, in CAs the mutual orientation that characterizes PPDT macromolecules is probably prevented, thus resulting in diminished interactions among them.

Consequently, new sets of solvent parameters have been proposed for each of the above aramid structures.

Accordingly, we suggest to reconsider also the choice of the solvents used for the synthesis of the corresponding hyperbranched analogs. Indeed, these macromolecules are known to have unique features due to their globular and dense architecture and to the large number of end groups and are generally characterized by relatively high solubility. On the basis of what found in this work, it should be emphasized that a proper study devoted to determine the best polymerization medium of these latter macromolecular compounds should also be undertaken.

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