Macromol. Symp. ***143****, 309–321 (1999)*

Hyperbranched Aramids by Direct Polyamidation of Two Reactant Sytems: Synthesis and Properties

Saverio Russo*, Alya Boulares[1], Andrea da Rin
Dipartimento di Chimica e Chimica Industriale, Università di Genova, via Dodecaneso 31, 16146 Genova, Italy

Alberto Mariani
Dipartimento di Chimica, Università di Sassari, via Vienna 2, 07100 Sassari, Italy

Maria Elisabetta Cosulich
Dipartimento di Biochimica, Università di Pavia, via Taramelli 3, 17100 Pavia, Italy

SUMMARY: Some A_2 + B_3 and A_3 + B_3 reagent pairs have been used for the direct polyamidation reaction leading, besides the network formation, to hyperbranched aramid structures. Depending on the chosen experimental conditions, variable amounts of a sol fraction having close similarities with the hyperbranched aramid structures derived from the polyamidation of AB_2 monomers, have indeed been obtained. Solubility of the sol fraction in various organic solvents, as well as its thermal properties and its capability of enzyme fixation, have been determined for the various systems under investigation. Future developments are envisaged.

Introduction

In a recent paper [1)] we have outlined the synthetic steps used for the preparation of some hyperbranched aromatic polyamides, originated either from an AB_2-type monomer or from two reactant systems (A_2 + B_3 or A_3 + B_3). Some preliminary results, related to the synthesis and characterization of the above structures, are therein reported.

---

[1] *present address: Institute of Materials Science, University of Connecticut, 97 North Eagleville Rd U-136, Storrs, CT 06269, USA*

CCC 1022-1360/99/$ 17.50+.50/0

The chosen synthetic method is based on the direct reaction between aromatic carboxylic groups, activated by triphenyl phosphite and pyridine, and aromatic amino groups. The original procedure, proposed by Yamazaki *et al.*2) in 1975, has been successfully improved later on by Higashi *et al.*3), Preston *et al.*4), and our group5-8). So far, the method has been almost exclusively applied to the synthesis of linear aramids, typically poly(*p*-phenylene terephthalamide) (PPDT) and poly(*p*-benzamide) (PBA).

A relevant improvement to the above synthetic route is represented by the so-called matrix polyamidation. It consists in the synthesis of aramids in presence of a second macromolecular compound, able to exert a strong influence on both the formation process and the properties of the polyamide, namely its molecular weight. For instance, the presence of poly(N-vinyl pyrrolidone) (PVP), solubilized in the reaction medium, has been found to strongly affect both PPDT synthesis and properties8,9). A polymer matrix-assisted synthesis is a well known phenomenon (template effect) in chain polymerization10), but is much less common and more difficult to be interpreted in step reactions, at least in the synthesis of rigid macromolecules. The lack of a clear description of the complex interactions between PVP and aramid growing chains has presently suggested to perform the syntheses of hyperbranched aramid structures only in neat systems. Therefore, the polyamidation reactions herein described have been carried out without a second polymer added and adopting the optimum reaction conditions found for neat linear systems6,7), with minor modifications when necessary.

As compared to the almost perfect architecture of dendrimers, it is well known that the hyperbranched polymer structures, because of their irregular growth, inevitably show some defects along the branches, thus causing a degree of branching (DB) intermediate between the values pertaining to linear (DB = O) and dendrimeric structures (DB = 1).

However, the ease of the one-step synthetic procedure and the many potential applications, the latter being not too different from those envisaged for the dendrimers, support the growing interest toward the development of new synthetic ways able to produce hyperbranched structures11-14). Moreover, the lower process costs and the possibility of an easier scale-up fully justify the present attention to this kind of approach. In particular, rigid structures, as those linked to hyperbranched aramids, can find new and interesting perspectives of application in various fields. For instance, their aromatic (highly hydrophobic) core, counterbalanced by the large number of hydrophylic end groups, may in principle allow solubility in both organic media and water solutions15).

So far, a few syntheses of dendrimeric and hyperbranched aramids have been reported in literature13,14,16-18). Most of the above structures, being based on the growth from a single (trifunctional) core, show full solubility in organic media in the whole conversion range. In the present paper, on the contrary, we have purposely explored the A_2 + B_3 and A_3 + B_3 systems, which should lead to polyfunctional non-linear structures, ultimately ending up with an infinite network only. A mention to this procedure has been outlined in [1] and (very briefly) in [18]. At intermediate conversions, there will be the formation of sol and gel fractions in various amounts, depending on the experimental conditions chosen[19]. Following the Flory-Stockmayer model, gelation will occur when the extent of reaction p exceeds a critical value p_c, linked to the monomer functionality φ. For systems containing two types of mutually reactive groups it has been estimated[20] that $p_c = [(\varphi_1 - 1)(\varphi_2 - 1)]^{-1/2}$. For our systems, therefore, p_c will be equal to *ca.* 0.7 for $\varphi_1 = 2$ and $\varphi_2 = 3$, and to 0.5 for $\varphi_1 = \varphi_2 = 3$.

Let us recall the most relevant points arising from a multifunctional polycondensation reaction[19]: at any extent of the reaction lower than p_c, a sol structure, formally very similar to the hyperbranched architecture arising from the polymerization of AB_x monomers, is the only species present. All molecules in the reaction medium are finite and a single (sol) phase is obtained. For $p > p_c$, sol and gel phases will coexist. The separation of the sol molecules from the gel fraction (for instance by filtration or centrifugation) will result in the isolation of hyperbranched structures.

The above approach to the synthesis of hyperbranched aramids structures is described in the present paper.

Experimental section

Chemicals. 1-Methyl–2-pyrrolidone (NMP), pyridine (Py), N,N-dimethyl acetamide (DMAc), lithium chloride, calcium chloride dihydrate, triphenylphosphite (TPP), *p*-phenylene diamine (PPD), *p*-nitroaniline, 5-aminoisophthalic acid, 4-nitrobenzoyl chloride, 1,3,5-benzene tricarboxylic acid (BTCA) and its chloride, terephthalic acid (TA) and *p*-aminobenzoic acid have been purified and stored as described in [1]. Pyromellitic acid, dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF) and 96% sulfuric acid have been used as received.

Synthesis of reactants. Full details of the experimental procedures for the synthesis of N,N',N''-*tris*(*p*-aminophenyl)-1,3,5-benzene triamide (TAPBT) and of N,N',N''-*tris*(*p*-carboxyphenyl)-1,3,5-benzene triamide (TCPBT) are given in [1]. TAPBT shows a melting point of 297-300 °C. ^1H NMR (δ ppm, DMSO-d_6, TMS): 10.40 (s, 3H), 8.65 (s, 3H), 7.48 (d, 6H, J = 9.1 Hz), 6.57 (d, 6H, J = 9.2 Hz), 4.96 (s, 6H). TCPBT has a melting point of 380 °C. ^1H NMR (δ ppm, DMSO-d_6, TMS): 13.36 (s, 3H), 10.97 (s, 3H), 8.85 (s, 4H), 8.73 (d, 4H, J =

2.4 Hz), 8.25 (t, 3H, J = 9.2 Hz). Structural formulae of TAPBT and TCPBT, together with those of the other reactants, are represented on Fig. 1. Double arrows show the chosen combinations of reagent pairs. A representation of some aramid structures originated from these syntheses is sketched in1).

Syntheses of hyperbranched aramids. Usually, hyperbranched aramids with sequences of amide groups along the branches analogous to those of PPDT have been prepared at 115 °C, following the modified Higashi's conditions (overall reactant concentration: *ca.* 0.17 mol.L^{-1}; TPP/acidic groups molar ratio: *c.a* 1.0; NMP/Py volume ratio: 5; LiCl % : 1.7 w/v; $CaCl_2$ % : 5 w/v). Again, experimental details on the synthetic procedures can be found in 1). When alternative set-ups have been employed, proper experimental conditions are adequately mentioned in the text.

Polymer characterization. Solution viscosity has been measured in Ubbelohde viscometers at 25 °C in various solvents, after filtration and separation of the gel fraction, if present. ^1H NMR spectra have been recorded at 300 MHz on a Bruker AM300 apparatus, in DMSO-d_6 at 25 °C. Differential Scanning Calorimetry analyses have been performed on a Mettler calorimeter apparatus, at the heating rate of 20 °C.min^{-1}. Weight loss of samples has been determined by thermogravimetric analysis, at the heating rate of 20 °C min^{-1} on a Perkin Elmer Thermal Analyzer Series 7.

Enzyme immobilization. The reaction between the activated carboxylic end groups of our hyperbranched aramids (in acetate buffer 0.1 M, pH = 4.7) and the amino groups of amylase has been performed using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) as coupling agent in large excess. The efficiency of the binding reaction is analyzed by protein determination with a BCA kit and the functional properties of the immobilized enzyme are investigated and compared to those of free enzyme.

V_{max} and Km from the Michaelis-Menten equation are evaluated in an enzymatic assay, where a coloured insoluble substrate is used. Namely, insoluble starch covalently labeled with the reactive dye Remazol Brilliant Bleu (RBB) is cleaved by α-amylase. The supernatant hydrolysis products are spectrophotometrically determined at 590 nm. The specific activity is expressed as U/mg of protein, where 1U of enzyme indicates the formation of one reducing group per minute at 25 °C.

Results and discussion

System PPD + BTCA. The various experimental conditions used in the synthesis of the hyperbranched aramid derived from this system are given in Tab. 1. Typically, the ratio

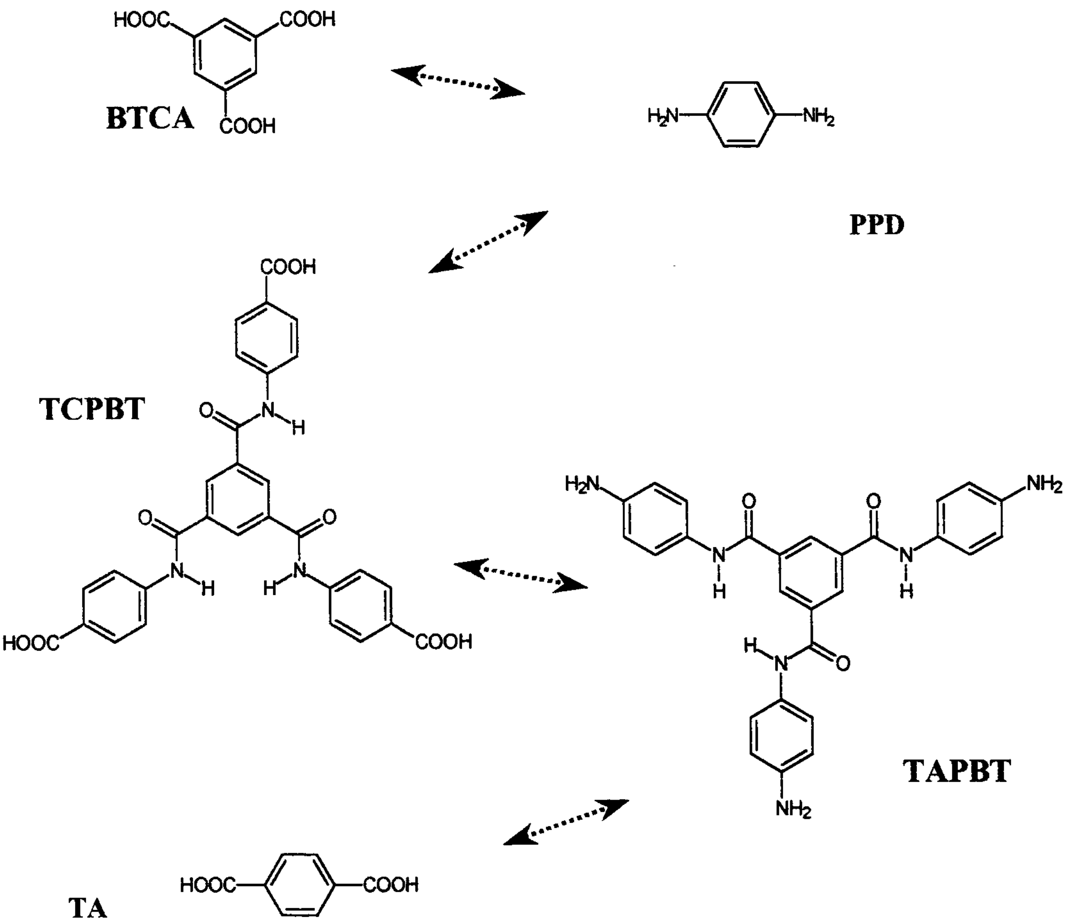


Fig. 1. Combination of reagent pairs

Tab.1. Experimental conditions for the synthesis of hyperbranched aramids

Sample code	**Reagent pair and overall concentration (mol/L)**	**TPP/-COOH molar ratio**	**t_p (h)**	**Physical gel formation (and time of, h)**
	PPD+BTCA			
Y1	0.20	1.09	3.0	Y (0.42)
Y2	0.20	1.09	4.0	Y (0.25)
Y8	0.16	1.09	3.5	Y (0.67)
Y9	0.20	1.09	2.5	Y (0.42)
Y12	0.20	1.09	7.0	Y (0.30)
Y31	0.24	0.67	3.0	Y (0.67)
Y32	0.20	1.09	0.5	N
	TAPBT+TA			
AB14	0.16	1.09	3.5	N
AB35	0.16	1.09	3.5	N
Y33	0.16	1.09	0.5	Y (0.08)
	PPD+TCPBT			
AB#3	0.16	1.09	3.0	Y (0.25)
AB40	0.16	1.09	3.5	N
AB50	0.16	1.09	3.0	Y (0.42)
Y35	0.16	1.09	0.5	N
	TAPBT+TCPBT			
AB#4	0.16	1.09	3.5	Y (1.00)
Y34	0.16	1.09	0.5	N

$-NH_2$/-COOH molar ratio = 1 (except for Y31, $-NH_2$/-COOH = 2/3); NMP/Py volume ratio = 5 (except for Y31, NMP/Py = 16); T_p = 115 °C (except for Y31, T_p = 80 °C); LiCl : 1.7 % (w/v) (except for Y31, LiCl : 6.7 % w/v); $CaCl_2$: 5.0 % (w/v) (except for Y31, $CaCl_2$: 0 %)

Tab.2. Extent of the insoluble fraction (%) in various solvent media

Sample code	**Reagent pair**	**t_p (h)**	**H_2SO_4**	**DMSO**	**NMP**	**DMAc**	**DMF**
Y32	PPD + BTCA	0.5	0	11	65	60	-
Y1	PPD + BTCA	3.0	60	60	60	60	82
AB#1	PPD + BTCA	3.5	98	100	100	100	100
AB12	TAPBT + TA	3.0	6	6	20	23	44
AB35	TAPBT + TA	3.5	55	56	-	-	-
AB14	TAPBT + TA	3.5	80	81	-	-	-
Y35	PPD + TCPBT	0.5	0	-	-	-	80
AB50	PPD + TCPBT	3.0	95	100	-	-	100

From the data of Tab. 2 a few considerations can be made:

i) solubility tests in H_2SO_4 are the most efficient and accurate method for determining the presence and the amount of the gel fraction;

ii) system PPD + BTCA: the sample Y32, produced in a reaction time, t_p, equal to 0.5 h, is completely soluble in H_2SO_4, whereas Y1 and AB#1 (t_p = 3.0 and 3.5 h, respectively) are partially (60%) or almost completely insoluble (98%);

between functional groups of the reactants has been fixed to 1. Modified Higashi's conditions have usually been applied, although a few syntheses have been purposely performed at lower or higher overall reactant concentrations, and lower TPP/-COOH molar ratios. In a single run (Y31) the inorganic salt dissolved in the reaction medium has been lithium chloride alone (6.7 w/v %). In the same run the ratio between $-NH_2$/-COOH groups has been fixed to 2/3, T_p to 80 °C, NMP/Py to 16 (v/v), in analogy with the experimental conditions used in recent literature for the preparation of hyperbranched aramids synthesized from the same reactants[18)]. It is interesting to note that in many cases a (presumably physical) gel is formed in the reaction medium after a short while, similarly to what happens during the synthesis of linear PPDT. In Tab. 1 the notation Y underlines gel formation in the specific system.

The physical gel in the linear system has been attributed to the formation of a labile network among polyamide chains, dissolved salts and solvent molecules, *via* ion-dipole interactions and hydrogen bonds. Analogous interactions may be also present in our $A_2 + B_3$ polymerizing system in which, in addition, chemical gelation will occur at the appropriate p_c value.

The complex pattern of the present syntheses is evidenced in Tab. 1 by the occurrence of no gel (N) formation in some experiments, thus suggesting a strong competition (of kinetic character) between the tendency to physical gel formation and that producing the hyperbranched structures and, ultimately, the network.

Systems PPD + TCPBT and TAPBT + TA. The relevant data for the above systems are also given in Tab. 1. Here again, the occurrence of a (presumably physical) gel does not appear to be reproducibile and can be reasonably considered in competition with the concurrent formation of hyperbranched structures. The fastest is the growth of higher generations of the above polymers (those assuming a close-to-globular structure), less probable is the physical gel formation, which requires the presence of strong intermolecular interactions.

System TAPBT+TCPBT. Tab. 1 shows the data pertaining to two runs carried out on this A_3+B_3 reagent pair.

Sol/gel fractions in various solvents. The extent of the formed network can be evaluated as a function of the conditions chosen for the reaction of a specific reagent pair. In general, the behaviour of these structures in various solvents represents an important aspect of the present work, inasmuch as it allows information not only on the kinetics of network formation, but also on the potential use of common organic solvents for both the characterization and the utilization of our hyperbranched aramids. Relevant data on the extent of the insoluble fraction are given in Tab. 2 and refer, for the sake of simplicity, only to some of the samples that have been prepared.

iii) system TAPBT + TA: the sample AB12, formed in 3.0 h of reaction, shows a much lower insoluble fraction (6%), as compared to the corresponding sample of the previous system (Y1). Its conversion rate, therefore, is slower. Between 3.0 and 3.5 h the gel formation grows very rapidly, as evidenced by the gel content of the samples AB35 and AB14. As could be reasonably expected, the reproducibility of solubilization data is rather poor: AB35 gives an insoluble fraction of 55%, AB14 of 80%. Indeed, in these rapidly changing experimental conditions, small kinetic differences may strongly affect the extent of gel fraction at a given reaction time;

iv) system PPD + TCPBT: the sample Y35 (t_p = 0.5 h) is completely soluble in H_2SO_4, whereas the sample AB50 (t_p = 3.0 h) is almost completely insoluble. From the above data, the latter system is characterized by the highest conversion rate.

As shown in Tab. 2, solubility data in DMSO almost exactly match, with minor fluctuations, the above data in H_2SO_4. The other organic solvents (NMP, DMAc, DMF) give less reproducible results, mostly because they are media in which aramid aggregates are present to a lower or greater extent, thus affecting precipitation equilibria. Their solubilization data, therefore, cannot be simply related to the gel fraction formation.

Solution viscosity. The sol fraction of our aramids has been characterized in terms of solution viscosity in H_2SO_4, DMF + 4 % LiCl and DMSO.

Relevant data are collected in Tab. 3.

Tab.3. Intrinsic viscosity values of the sol fraction at 25°C

Sample code	Reagent Pair	[η] in H_2SO_4 (dL/g)	[η] in DMF+ 4% LiCl (dL/g)	[η] in DMSO (dL/g)
Y1	PPD+BTCA	1.02	1.22	1.08
Y2	PPD+BTCA	0.89	3.80	0.88
Y8	PPD+BTCA	1.27	4.90	1.64
Y9	PPD+BTCA	1.17	5.00	0.93
Y31	PPD+BTCA	0.87	-	-
Y32	PPD+BTCA	0.21	-	-
AB35	TAPBT+TA	0.08	-	-
AB#3	PPD+TCPBT	-	1.85	-
AB50	PPD+TCPBT	0.50	0.51	-
Y35	PPD+TCPBT	-	-	0.18
AB#4	TAPBT+TCPBT	-	2.55	-
Y34	TAPBT+TCPBT	<0.1	-	-

[η] values obtained in DMF + 4 % LiCl solutions are anomalously high as compared to those obtained in the other solvents and are an indirect proof of a strong polymer aggregation in the above medium. Kim$^{17i)}$ has described similar phenomena for his hyperbranched aramids in the same solvent medium.

Glass transition temperatures and thermogravimetric behaviour of the hyperbranched aramids (soluble fraction). A comparison between the various structures of our hyperbranched aramids and their properties (for instance, thermal behaviour) can be attempted by taking in account the following two parameters:

i) regularity rules for the description of amide sequences along the branches;

ii) number of aromatic nuclei between trifunctional branching points; for instance, the notation 1L(Ar) means that only one aromatic ring is present within the branches.

The classification of our samples has been done on this basis.

T_g values for our aramids are given in Tab. 4. It is evident that ordered structures in terms of amide sequences along the branches (namely, those analogous to PPDT) are characterized by T_g values (152 – 153 °C) higher than the more 'disordered' ones. The lowest T_g value corresponds to the most 'disordered' sequence of amide groups.

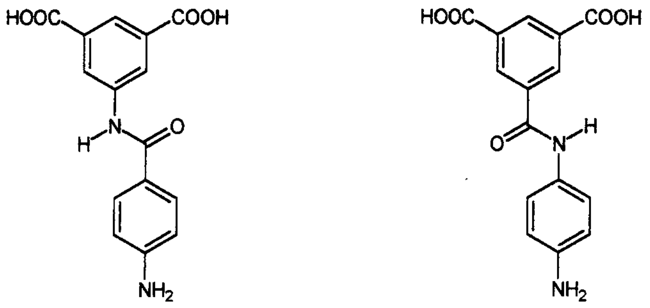
'Disordered' sequences have here the meaning of more complex regularity rules describing the running of -CO- and -NH- groups in the amide sequences along the branches. The net effect of these rules means in practice a local 'disorder' favouring T_g lowering.

A comparison with T_g values of hyperbranched aramids arising from AB_2 monomers [21)] (ABZAIA and ABAMIA, see Fig. 2) supports the relevance of ordered sequences in determining the T_g range of values. Both the structure analogous to PPDT (in terms of amide sequence) and that analogous to PBA show T_g values of 152 – 153 °C[21)]. No effect whatsoever on T_g values is linked to the number of aromatic nuclei (and therefore to the distance) between trifunctional branching points, as evidenced on Tab. 4. For the sake of comparison, both AB_2 – type aramids quoted above have an L(Ar) value of 1 and confirm the aforementioned statement[21)].

Thermogravimetric analysis in nitrogen atmosphere shows good thermal stability for all samples up to 350 °C. Their stability in oxygen is obviously a little lower (*ca.* 250 °C).

Tab.4. Glass transition temperatures of the sol fractions

Sample code	**Reagent pair**	**Sequence analogy of amide groups**	**L (Ar)**	**T_g (°C)**
Y 32	PPD + BTCA	PPDT	1	153
Y 33	TAPBT + TA	PPDT	3	152
Y 35	PPD + TCPBT	'disordered' PPDT	3	136
Y 34	TAPBT + TCPBT	'disordered' PPDT	2	128



ABZAIA **ABAMIA**

Fig. 2: AB_2 monomer systems

Amylase fixation. The formation of rigid, hyperbranched polymeric materials is potentially relevant for enzyme fixation. Hyperbranched structures with a higher concentration of suitable end groups onto or near the outer surface seem ideal in this respect. We have tested the properties of our hyperbranched aramids in terms of their capability not only to link a specific enzyme (amylase), but also to stabilize its activity, once linked to the rigid support represented by the aramid.

Preliminary data on enzyme fixation and activity are given in Tab. 5. It can be noticed that the carboxylic groups of hyperbranched aramids are reactive in our experimental conditions and able to bind the enzyme up to *ca.* 0.8 mg of protein/mg of support. As compared to the most common insoluble supports for enzymes, the linking ability of our hyperbranched aramids is almost an order of magnitude higher. The properties of the immobilized enzyme have been investigated and compared to those of the free enzyme. Changes in V_{max} and Km (see Experimental) have been measured for the immobilized amylase. As shown in Tab. 5, the decrease of Km values in Y34 and AB50 underlines a higher affinity between the catalytic site of the enzyme and the substrate for these systems. The sample AB 50, characterized by a distance between the trifunctional branching points equal to 3L(Ar), shows a greater enzymatic activity than Y34, characterized by L(Ar) equal to 2, and Y1 and Y8, characterized by L(Ar) equal to 1. It seems, therefore, that a less compact structure makes easier the access to the active site of amylase. Furthermore, the lower degree of order for the samples AB50 and Y34, in terms of amide group sequences, may significantly contribute to the above enhancement of enzymatic activity. On the basis of the experimental procedure used, the linking capability, on the other hand, is related only to the concentration and availability of carboxylic groups on the outer surface of the polymer.

Molecular modeling of the various structures could be very helpful in this respect and able to explain the above differences..

Tab.5. Amount of amylase linked to hyperbranched aramids and bioactivity retention

Sample code	**Reagent pair**	**L(Ar)**	**linked amylase %**	**Specific activity (U/mg of protein)**	**Km[#] (mg/mL)**
Y 8	PPD + BTCA	1	81.5	320	26
Y 1	PPD + BTCA	1	79.9	350	16.7
Y34	TAPBT+TCPBT	2	71.8	332	2.4
AB50	PPD+TCPBT	3	75.0	315	1.8
α-amylase (free enzyme)				*400*	*5.8*

[#] Michaelis-Menten constant is expressed as starch-RBB concentration (mg/mL)

Conclusion

As far as the direct synthesis of aramids is concerned, the polyfunctional step polymerization of $A_2 + B_3$ and $A_3 + B_3$ systems can open some interesting perspectives for the development of new structures, and therefore of properties and applications for this class of hyperbranched polymers. The sol fractions present before and during network formation will have a hyperbranched structure, rather similar to that derived from AB_x monomers. The one-step preparation, the existence of linear units (or failure sequences), the polydispersity in both molecular weight and branching emphasize the close similarities between the two structures. Solubility in common organic solvents, very low solution viscosities, good thermal properties and a great ability to link enzymes, such as amylase, are the most relevant results obtained so far for the aramid structures described in the present paper. Future developments in several areas are envisaged.

Acknowledgements

The helpful collaboration of Dr. Stefania Bisbano and Miss Sara Pasquali on various aspects of the present work has been highly appreciated. One of the authors (A.B.) thanks European Community for its financial support as a postdoctoral TMR grant (Contract ERBFMBICT960844). MURST funds are gratefully acknowledged.

References

1) S. Russo, A. Boulares, A. Mariani, *Macromol. Symp.* **128**, 13 (1998)

2) N. Yamazaki, F. Higashi, J. Kawabata, *J. Polym. Sci., Polym. Chem. Ed.* **13**, 1373 (1975)

3) F. Higashi, S.-I. Ogata, Y. Aoki, *J. Polym. Sci., Polym. Chem. Ed.* **20**, 2081 (1982)

4) W.R. Krigbaum, R. Kotek, Y. Mihara, J. Preston, *J. Polym. Sci., Polym. Chem. Ed.* **22**, 4045 (1984); ii) *J. Polym. Sci, Polym. Chem. Ed.* **23,** 1907 (1985)

5) S. Russo, A. Mariani, V.N. Ignatov, I.I. Ponomarev, *Macromolecules* **26**, 4984 (1993)

6) A. Mariani, S.L.E. Mazzanti, S. Russo, *Can. J. Chem.* **73**, 1960 (1995)

7) S. Russo, A. Mariani, S.L.E. Mazzanti, *Macromol. Symp.* **118**, 73 (1997)

8) S. Russo, A. Mariani, S.L.E. Mazzanti, G. Ruggeri, G. Conio, *Macromol. Symp.* **122**, 1 (1997)

9) S. Russo, A. Mariani, M. Piacentini, P. Sozzani, R. Simonutti, manuscript in preparation

10) S. Polowinski, Template Polymerization, Chem. Tech. Publ., Toronto, 1997

11) D.A. Tomalia, D.M. Headstrand, L.R. Wilson 'Dendritic Polymers' in Encyclopedia of Polymer Science and Engineering, 2nd Edition, Vol. 1, pp. 46-92, Wiley Interscience Publ., New York, 1986

12) i) D.A. Tomalia, A.M. Naylor, W.A. Goddard, III, *Angew. Chem. Int. Ed. Engl.* **29**, 138 (1990); ii) D.A. Tomalia, P.R. Dvornic, 'Dendritic Polymers, Divergent Synthesis (starburst polyamidoamine dendrimers)' in Encyclopedia of Polymeric Materials, pp. 1814-1830, CRC Press Inc., Boca Raton, 1996

13) Y.H. Kim, 'Highly Branched Polymers' in Encyclopedia of Polymeric Materials, pp. 3049-3053, CRC Press Inc., Boca Raton, 1996

14) J.M.J. Fréchet, C.J. Hawker, 'Synthesis and Properties of Dendrimers and Hyperbranched Polymers' in Comprehensive Polymer Science, 2nd Suppl., Ch. 3, pp. 71-132, S.L. Aggarwal, S. Russo eds, Pergamon (Elsevier), Oxford, 1996

15) Y.H. Kim, O.W. Webster, *J. Am. Chem. Soc.* **112**, 4592 (1990)

16) i) P.M. Bayliff, W.J. Feast, D. Parker, *Polym. Bull.* **29**, 265 (1992); ii) S.C.E. Backson, P.M. Bayliff, W.J. Feast, A.M. Kenwright, D. Parker, R.W. Richards, *ACS Polymer Prepr.* **34(1)**, 50 (1993); iii) *Macromol. Symp.* **77**, 1 (1994)

17) i)Y.H. Kim, *J. Am. Chem. Soc.* **114**, 4947 (1992); ii) *Adv. Mater.* **4**, 764 (1992); iii) *ACS Polymer Prepr.* **34(1)**, 56 (1993); iv) *Macromol. Symp.* **77**, 21 (1994); v) *Polym. Mat. Sci. Eng.* **73**, 175 (1995)

18) M. Jikei, Y. Gang, C.S. Myun, M. Kakimoto, *ACS PMSE Proc.* **77**, 200 (1997)

19) P.J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, 1953

[20] C.W. Macosko, D.R. Miller, *Macromolecules* **9**, 199 (1976)

[21] S. Russo, S. Bisbano, A. Mariani, M.E. Cosulich, manuscript in preparation