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SYNTHESIS OF HYPERBRANCHED AROMATIC POLYAMIDES BY DIRECT POLYCONDENSATION

Saverio Russo*, Alya Boulares

Dipartimento di Chimica e Chimica Industriale, Università di Genova,
via Dodecaneso 31, 16146 Genova, Italy

Alberto Mariani

Dipartimento di Chimica, via Vienna 2, 07100 Sassari, Italy

Abstract : Some hyperbranched aromatic polyamides have been synthesized by direct polycondensation using the modified Higashi's method. Structures of the above polymers have been realized taking in proper account the analogies with amide group sequences of poly(*p*-phenyleneterephthalamide) (PPDT) and poly(*p*-benzamide) (PBA). Therefore, AB_2- type monomers as well as suitable combinations of different bi- and trifunctional reactants ($AA + B_3$) (e.g., *p*-phenylenediamine + trimesic acid or other trifunctional acids) have been considered. For the latter systems, network formation has been minimized. In the present paper, our results on their direct polyamidation together with some preliminary characterization data on the resultant hyperbranched aramids are given.

INTRODUCTION

The synthesis of high molecular weight aromatic polyamides is generally carried out by means of the reaction between aromatic amines and activated derivatives of carboxylic acids, namely their chlorides. In particular, PPDT of intrinsic viscosity, $[\eta]$, equal to 6-7 $dL.g^{-1}$ is industrially obtained with this method. On the laboratory scale, the above reaction is often replaced by the *direct synthesis*, in which aromatic carboxylic acids, activated by triphenyl

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phosphite and pyridine, are directly used. In our research group this alternative route has been thoroughly developed and optimum reaction conditions for direct polyamidation have been found. Indeed, under certain experimental conditions (extensive purification procedures and proper choice of reaction parameters), PPDT of [η] up to 10.1 $dL.g^{-1}$ has been synthesized (Refs. 1-3).

When a polymer matrix-assisted synthesis has been carried out, linear PPDT of [η] up to 14.2 $dL.g^{-1}$ has been obtained (Ref. 4). Moreover, it has been shown in the same paper that the molecular weight of the matrix polymer strictly control PPDT molecular weight. After these successful attempts, we tried to apply the above method to the synthesis of hyperbranched aromatic polyamides having a molecular structure, in terms of sequence of CO and NH groups along the branches, similar to that of the linear aramids of our interest, namely PPDT and PBA. These highly-branched polymers have shown some peculiar features which are now under investigation. Because of the rather high degree of branching as well as of the large number of terminal groups (micellar-like structure), the solubility of these compounds in several organic solvents resulted enhanced. At the same time, network formation from AA + B_3 systems, due to the specific experimental conditions chosen, has been minimized. Their potential exploitation in various fields of application is underway and will be reported later on. In the present paper our results related to the synthesis of hyperbranched aromatic polyamides, together with some preliminary data on their characterization, are given.

EXPERIMENTAL SECTION

Chemicals. 1-Methyl-2-pyrrolidone (NMP) (Aldrich) was refluxed over CaH_2 and distilled under vacuum, then refluxed over P_2O_5 and distilled (Ref. 2); pyridine (Py) (Fluka) was first refluxed under inert atmosphere in the presence of sodium hydroxide and distilled, then refluxed over CaH_2, distilled and stored in dark flask over molecular sieves; N,N-dimethylacetamide (DMAc) (Fluka) was shaken with barium oxide (BaO) for several days, then refluxed in presence of BaO, fractionally distilled under reduced pressure and stored in dark flask over molecular sieves (Ref. 5); lithium chloride (Riedel de Haen) and calcium chloride dihydrate (Fluka) were dried under vacuum for 24 h; triphenylphosphite (TPP) was purified by fractional distillation under vacuum; *p*-phenylenediamine (PPD) (Fluka) was purified by sublimation under vacuum over silica gel before use and *p*-nitroaniline was purified by crystallization from acetone; 5-aminoisophthalic acid (Fluka), 4-nitrobenzoyl chloride (Aldrich), 1,3,5-benzenetricarboxylic acid chloride (Aldrich) and trimesic acid (1,3,5-benzenetricarboxylic acid, BTCA) (Fluka) were used as received; *p*-aminobenzoic acid (Fluka) was dried under vacuum at 100°C.

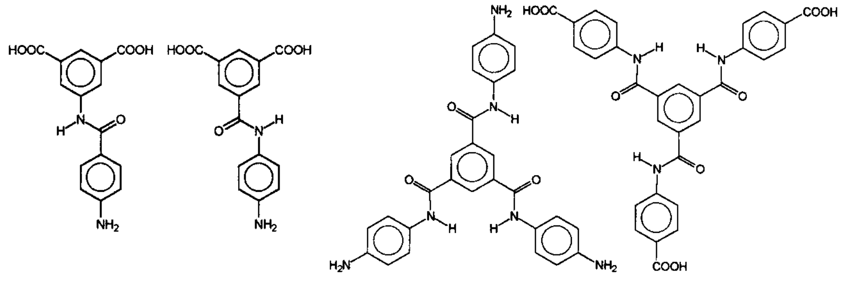
Synthesis of Monomers and Reactants

The nomenclature distinction between reactants and monomers has been reported and justified elsewhere (Ref. 6).

Synthesis of 5-(4-aminobenzoylamino)isophthalic acid (ABZAIA) (Fig. 1, Formula 1). The followed protocol for the synthesis of ABZAIA has been taken from Ref. 7. A well-stirred mixture of 5-aminoisophthalic acid in DMAc, blanketed with nitrogen, is heated to 80°C until complete dissolution of the compound. Then the solution is cooled to about 10°C and a solution of 4-nitrobenzoyl chloride in DMAc added dropwise. The reaction is maintained at low temperature for 3 h and the final mixture poured into water. The precipitate formed is filtered, extracted with hot water and dried under vacuum. After recrystallization in methanol, the dried product is added in one step to a well stirred mixture of 0.3 mole of stannous chloride, 125 mL of fuming hydrochloric acid and 125 mL of glacial acetic acid, cooled to 10°C. The temperature is slowly raised to 80°C and, after ca. 12 h of reaction, the mixture poured into water, the precipitate filtered off, washed several times with hot water and finally dried at 80°C under vacuum. The resultant product is recrystallized from N,N-dimethylformamide (DMF)/H_2O = 1/1. The sequence of functional groups -COOH, -CO-NH- and -NH_2 is reminiscent of the arrangement of amide links in PBA repeat unit.

Synthesis of 5-(4-aminobenzamido)isophthalic acid (ABAMIA) (Fig. 1, Formula 2). The monomer ABAMIA is synthesized by two ways, both leading to the 3,5-dimethyl-benzamido-4-nitrobenzene (DMBN). DMBN can be prepared from 3,5-dimethylbenzoyl chloride and *p*-nitroaniline in DMAc, the aryloyl chloride being realized from its corresponding acid by the well known reaction with thionyl chloride. The other way consists in the direct condensation of BTCA with *p*-nitroaniline in Higashi's conditions (Refs. 8,9), giving DMBN with a higher yield as compared to the first method. DMBN methyl groups are then oxidized following the protocol given in Ref. 9 and the nitro end-groups reduced as described in Ref. 7. This leads to a trifunctional monomer with two acid and one amino functions with a sequence of the functional groups -COOH, -NH-CO- and -NH_2 able to give rise to a structure, in the arrangement of amide links, similar to PPDT repeat unit.

Synthesis of N,N',N"-tris(*p*-aminophenyl)-1,3,5-benzenetriamide (TAPBT) and N,N',N"-tris(*p*-carboxyphenyl)-1,3,5-benzenetriamide (TCPBT) (Fig. 1, Formulae 3 and 4, respectively). These two trifunctional reactants can be prepared in DMAc solution below room temperature by a Schotten-Baumann type reaction. TAPBT is synthesized from 1,3,5-benzenetricarboxylic acid chloride and *p*-nitroaniline, followed by the reduction of the nitro end-groups by stannous chloride in presence of fuming hydrochloric acid and glacial acetic acid, as described above; the product is filtered off, washed with hot water and dried under vacuum. TCPBT is the product of condensation of 1,3,5-benzenetricarboxylic acid chloride with *p*-aminobenzoic acid; after the reaction in DMAc, the mixture is poured into methanol, the precipitate is filtered off and dried under vacuum.



1 *2* *3* *4*

Fig 1: Trifunctional monomers and reactants.

1: ABZAIA:; *2*: ABAMIA; *3*: TAPBT; *4*: TCPBT:

Hyperbranched Polymers Synthesis. For all hyperbranched structures, the experimental conditions chosen for the synthesis are very close to those mentioned in previous papers of ours on the synthesis of linear polymers in modified Higashi's conditions (Refs. 2,3). Thus, the overall concentration of reactants or monomers is ca. 0.16 mol.L^{-1} in the mixture of NMP and Py (5/1, v/v); the concentration of TPP is in slight excess as referred to the overall concentration of carboxylic acid functions; the amounts of LiCl and $CaCl_2$ are 1.7% and 5% w/v of solvents, respectively. Oxygen traces are preliminary removed from the reaction medium by several cycles of vacuum and inert gas. The reaction is carried out at 115°C and a clear gel is always formed after 15 up to 30 min. After 3-4 hours of reaction, the polymer obtained is ground in a blender in presence of methanol. The product is washed with boiling methanol and dried overnight in a vacuum oven at 80°C.

RESULTS AND DISCUSSION

As described in the Experimental, different structures of hyperbranched aramids have been synthesized:

a) by using the above AB_2 monomers 1 or 2 alone,

b) by using, in combination with terephthalic acid, the A_3 reactant 3, or in combination with *p*-phenylenediamine, the A_3 reactant 4 or BTCA. The combination of 3 and 4 has also been attempted. In this case, gel point achievement and network formation would normally be expected as predicted by Flory (Ref. 10). However, that was not the case in our experimental conditions. It seems that the physical gel formed at the very beginning of the reaction prevents or delays network formation, maximizing the production of hyperbranched, soluble structures.

Two of the resultant structures are sketched on Fig. 2. The minimum length between the trifunctional cores varies between 1L(Ar) and 3L(Ar) from one structure to another, according to the monomers used and to the combinations made from the different reactants, 1L(Ar) corresponding to the length of one segment with only one aromatic core. These lengths can be easily measured following Aharoni's treatment concerning similar structures (Ref. 11). Differences in L(Ar) among the various hyperbranched aramids would strongly influence their behavior in solution.

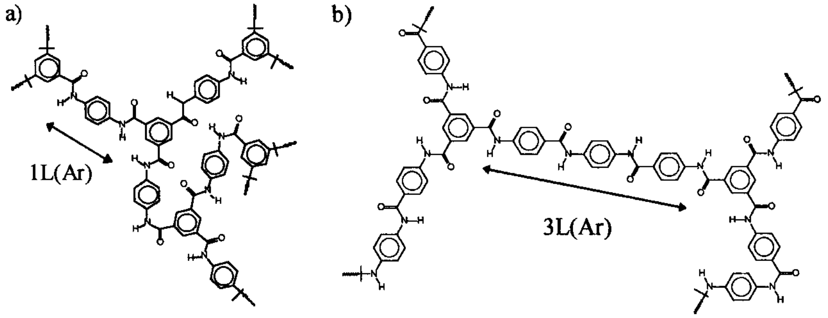


Fig. 2: Aramid structures formed by direct synthesis from:
a) BTCA and PPD; b) TCPBT and PPD.

These highly branched polymers present a far better solubility than their homologous linear polymers in amide solvents, such as N,N-dimethylformamide or dimethylsulfoxide. Thus, the viscosity measurements of our hyperbranched aramids were made in that solvent (either neat or added with 3% LiCl) at 30°C. Namely, the aramids derived from TCPBT+PPD and TCPBT+TAPBT required addition of LiCl (3% w/v) in order to be solubilized. The values of η_{inh} and [η] *for the various hyperbranched structures are given in* Table 1. *In order to compare* [η] values for the four structures of Table 1 it is necessary to refer to the last column, where data related to DMF+3% LiCl are collected. The regular increase of viscosity going from the more closely packed ABZAIA to the larger irregular 'globules' is evident.

The evaluation of DB (degree of branching) for the five structures is under way and will be reported in a short time (Ref. 12).

Table 1 : Viscosity values of some hyperbranched polymers (T = 30°C)

Reactant Type		$[\eta]_{DMF}$ ($dL.g^{-1}$)	$[\eta]_{DMF+3\% LiCl}$ ($dL.g^{-1}$)
AB_2	ABZAIA	0.36	0.44
$AA + B_3$	PPD + BTCA	1.1	-
$AA + B_3$	PPD + TCPBT	-	1.85
$A_3 + B_3$	TCPBT + TAPBT	-	2.75

For the hyperbranched aramid derived from ABZAIA some SEC analyses have been performed both in neat DMF and in DMF+3% LiCl. A very large aggregation phenomenon has been found in DMF, with apparent molecular weights (expressed as PS equivalents) near to 2.10^6. The addition of LiCl is able to destroy, at least in part, these aggregates, giving an apparent molecular weight of ca. 10^5. MALDI-TOF data suggest values of Mw of ca. 53,000 and Mn of ca. 11,400, corresponding to ca. 40 monomer units, i.e. in between the third and the fourth generation for a perfect dendrimeric structure (Ref. 13). The relatively low [η] value (0.36 $dL.g^{-1}$ in DMF, 0.44 $dL.g^{-1}$ in DMF+3% LiCl) might be considered an indirect proof of the rather low concentration of residual unreacted sites entrapped within the hyperbranched structure or, in other words, of failure sequences, as described by Fréchet and Hawker (Ref. 13). However, the polydispersity index, around 4.6, underlines a quite broad distribution of molecular weights, generated by a large amount of defects.

The mesophasic behavior of some hyperbranched aramids in solution of organic solvents has been investigated and, at least for one system, a sharp shear birefringence has been found for a 15% (w/v) gel-like solution in DMF + 3% (w/v) of LiCl. This characteristic behavior has already been noticed by Kim (Refs. 14,15) in NMP solutions of the hyperbranched aromatic polyamide made from 5-aminoisophthalic acid derivatives. A more detailed investigation on these mesophases and their potential liquid crystalline behavior is under way (Ref. 12).

CONCLUSION

In our laboratory a method has been developed for the direct synthesis of new hyperbranched aramids. These materials show a structure and a behavior rather close to those derived from a pure dendrimeric architecture. The sequence of amide groups along the chains is analogous to that of their linear homologues (PPDT and PBA). The enhanced solubility of hyperbranched aramids in organic solvents may open interesting perspectives in the near future as potential substitutes of the corresponding linear polymers in many applications. A full report on the subject will soon appear elsewhere (Ref. 12).

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REFERENCES

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

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

(3) S. Russo, A. Mariani, S.L.E. Mazzanti, *Macromol. Symp.* in press

(4) S. Russo, A. Mariani, S.L.E. Mazzanti, G. Ruggeri, G. Conio, *Macromol. Symp.* in press

(5) D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemicals*, 3rd Ed, Butterworth-Keinemann Ltd., Oxford (1988)

(6) F. Parodi, S. Russo, *Comprehensive Polymer Science*, Vol. 5, Pergamon, Oxford (1989)

(7) A.E. Lozano, J. Preston, J. De Abajo, J.G. De La Campa, *Polym. Prepr.* **34**(2), 524 (1993)

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

(9) A.E. Lozano, J. De Abajo, J.G. De La Campa, J. Preston, *J. Polym. Sci., Polym. Chem. Ed.* **33**, 1987 (1995)

(10) P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca (1953)

(11) S.M. Aharoni, S.F. Edwards, *Adv. Polym. Sci.* **118**, 1 (1994)

(12) S. Russo, A. Mariani, A. Boulares, E. Dossi, manuscript in preparation

(13) J.M.J. Fréchet, C.J. Hawker, *Comprehensive Polymer Science*, 2nd Suppl. Vol., Ch. 3, p. 71f, Pergamon, Oxford (1996)

(14) Y.H Kim, *Polym. Mat. Sci. Eng.* **73**, 51 (1995)

(15) Y.H Kim, *Macromol. Symp.* **77**, 21 (1994)