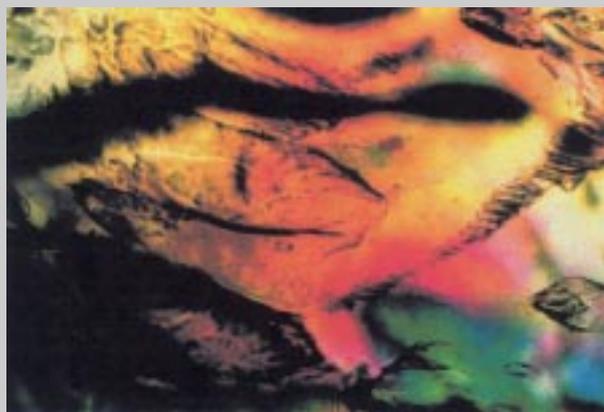


Full Paper: A hyperbranched aromatic polyamide has been prepared by direct polycondensation of 5-(4-aminobenzoylamino)isophthalic acid (ABZAIA), using the modified Higashi's method. The resultant polymer is soluble in aprotic polar solvents such as DMF, DMAc, NMP, and DMSO. Intrinsic viscosities of poly(ABZAIA) samples, measured in sulfuric acid at 25 °C, are in the range between 0.2 and 0.3 dL · g⁻¹. Glass transition temperature (T_g) is placed around 150 °C and onset temperature of thermal decomposition at about 275 °C. Full molecular weight distribution, evaluated by a SEC apparatus equipped with three different detectors, gives \bar{M}_w values in the range between 55 000 and 300 000 g · mol⁻¹, with a polydispersity index, \bar{M}_w/\bar{M}_n , relatively large and generally around 3–4. Poly(ABZAIA), synthesized in suitable experimental conditions, shows rather low values of Mark-Houwink a constant. Together with $[\eta]$ data, these a values are consistent with a hyperbranched, close-to-globular shape of our polymer. Highly concentrated polymer solutions (>40 wt.-%) in NMP show shear birefringence under polarized light. The specific surface area of the powdered material, calculated by nitrogen adsorption/desorption isotherm, is ca. 40 m² · g⁻¹.



Polarized light optical micrograph of a poly(ABZAIA) solution in NMP (60 wt.-%) under shear at room temperature.

Synthesis, characterization and properties of a hyperbranched aromatic polyamide: poly(ABZAIA)

Orietta Monticelli,*¹ Raniero Mendichi,² Stefania Bisbano,¹ Alberto Mariani,³ Saverio Russo¹

¹ Dipartimento di Chimica e Chimica Industriale, Università di Genova, via Dodecaneso 31, 16146 Genova, Italy
Fax: +39-010 3536199; E-mail: orietta@chimica.unige.it

² Istituto di Chimica delle Macromolecole C.N.R., via Bassini 15, 20133 Milano, Italy

³ Dipartimento di Chimica, Università di Sassari, via Vienna 2, 07100 Sassari, Italy

Introduction

Recently, dendritic and hyperbranched polymers have attracted increasing attention due to their unique physical and chemical properties.^[1–3] In particular, the one-step synthesis of hyperbranched (HB) structures overcomes most of the problems associated with the tedious, multi-step dendrimer preparation, while retaining a large part of the most important features, typical of highly regular dendrimeric structures.

Several polymerization methods (e.g., polycondensation,^[1–5] polyaddition,^[3,6,7] ring-opening,^[3,8] etc.) have been used to prepare a wide variety of hyperbranched polymers, such as polyphenylenes,^[9] aromatic polyesters,^[5] polyurethanes^[10,11] and aromatic polyamides.^[12,13] Among them, hyperbranched aramids are very interesting, being able to retain some excellent properties

of their linear homologues (e.g. heat and flame resistance), supplemented by an easier processability. However, only very recently additional synthetic approaches to HB aramids have been reported in literature.^[14–19]

Kim synthesized hyperbranched aromatic polyamides by self condensation of either 3,5-diaminobenzoyl chloride or 3-aminoisophthaloyl chloride, the latter showing birefringence in an amide solvent (NMP).^[12,14] Both thermal and direct polymerization of AB₂ monomers have been used by Kakimoto et al.^[16,17] to prepare HB aromatic polyamides. Recently, hyperbranched aramids have been synthesized also from commercial A₂ (diamine) + B₃ (triacid) reagent pairs.^[15,18,19] Indeed, in a preliminary paper^[15] we have described the synthesis of HB aramids either from AB₂-type monomers or from two-reactant systems (A₂ + B₃, A₃ + B₃ and A₂ + B₄). The above poly-

mers have been used as supports for α -amylase immobilization, offering an interesting approach to potential industrial applications of these materials^[20].

In the present paper we have focused our attention on the HB aramide directly synthesized from 5-(4-aminobenzoylamino)isophthalic acid. The polymer has been prepared using the procedure reported previously^[15] with minor modifications. Various characterization techniques have been used in order to evaluate polymer properties. In particular, SEC method provided full molecular weight distribution (MWD) of our poly(ABZAIA) samples, throwing some light on their shape changes as functions of \bar{M}_w . Moreover, liquid crystalline properties of highly concentrated polymer solutions have been explored.

Experimental

Materials

1-Methyl-2-pyrrolidone (NMP), pyridine (Py), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), lithium chloride, calcium chloride, triphenyl phosphite (TPP), 5-aminoisophthalic acid and 4-nitrobenzoyl chloride (all from Aldrich) were purified and stored as described elsewhere.^[15] The catalyst used in the hydrogenation reaction was palladium on alumina at a Pd concentration of 10 wt.-% (Aldrich).

Monomer synthesis

The monomer, shown in Fig. 1, was synthesized substantially following the procedure given elsewhere,^[15] only changing the final hydrogenation procedure in order to transform the nitro group of 5-(4-nitrobenzoylamino)isophthalic acid into the amino one. Namely, instead of using an acid solution of stannous chloride, a catalytic hydrogenation was accomplished. The reaction was carried out at room temperature in a hydrogen atmosphere for 12 h using DMAc as the solvent. The concentration of the catalyst used (Pd on alumina), was 10 wt.-% with respect to the monomer. Then, the reduced product was filtered off to separate it from the catalyst powder. The clear solution was poured into water, and the precipitate

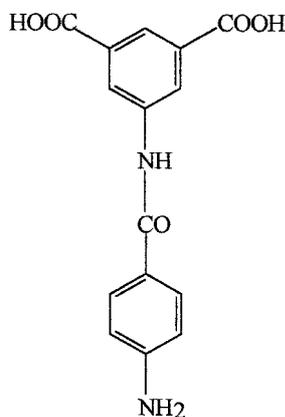


Fig. 1. ABZAIA monomer.

filtered off, washed several times with hot water and finally dried at 80 °C under vacuum.

ABZAIA monomer shows a melting point of 283 °C.

¹H NMR at 300 MHz (DMSO-*d*₆): δ = 10.11 (s, 1H), 8.66 (d, 2H), 8.17 (t, 1H), 7.77 (d, 2H), 6.62 (d, 2H).

IR (KBr): broad absorption band from 3700 to 2500; 1660 (amide C=O); 1511 (CNH); 1590, 1422 (aromatic); 1331; 1286; 1247; 802; 766 cm⁻¹. The absorption bands at 1563 cm⁻¹ (asymmetric CO₂ stretch) and 1393 cm⁻¹ (symmetric CO₂ stretch) could be due to the zwitterion.

Synthesis of HB aramide

The hyperbranched aramide samples were synthesized following modified Higashi's conditions.^[21] A complete justification and description of this modified method are given elsewhere.^[22] Here we only mention that the monomer concentration was 0.14 M in the 5:1 v/v mixture of NMP and Py, containing also 6.7 wt.-% LiCl; [TPP]/[COOH] molar ratio was 1.09, except for sample MS5 ([TPP]/[COOH] = 2.00); T_{pol} was settled at 115 °C and t_{pol} at 3 h.

Characterization techniques

The solution viscosity was measured in a suspended level Ubbelohde viscometer at 25 °C in 96% H₂SO₄. Differential Scanning Calorimetry (DSC) analyses were performed on a Mettler calorimetric apparatus, mod. TC10A, at a heating rate of 10 °C · min⁻¹. Weight loss of samples as a function of temperature was determined by thermogravimetric analysis, in nitrogen atmosphere at a heating rate of 20 °C · min⁻¹, on a Perkin Elmer Thermal Analyzer Series 7. Porosity measurements were performed on an ASAP 2010 Micromeritics apparatus. Optical properties of poly(ABZAIA) solutions were followed by a microscope Polivar Pol. Reichert Jung. SEC measurements were carried out on a multi-detector SEC system, based on a Waters Alliance 2690 separation module equipped with a differential refractometer, a single capillary viscometer (SCV) and a multi-angle laser light scattering detector (MALS). Characteristics and performances of the multidetector SEC-MALS-SCV system have been described elsewhere,^[23] including references quoted therein. A column set based on four styragel columns from Waters (HR5, HR4, HR3 and HR0.5; 36 000 theoretical plates) was used at 50 °C, with DMF + 0.5 M LiCl as mobile phase (flow rate: 0.7 mL · min⁻¹; injection volume: 300 μ L). dn/dc was measured by a differential refractometer (Cromatix KMX-16) and found equal to 0.198 mL · g⁻¹.

IR (KBr) of poly(ABZAIA): broad absorption band from 3700 to 2500, 1711 (acid C=O); 1652 (amide C=O); 1511 (CNH); 1591, 1447 (aromatic); 1319; 1282; 1245; 956; 820; 759; 687 cm⁻¹.

Results and discussion

Direct polycondensation of 5-(4-aminobenzoylamino)isophthalic acid and purification of the reaction product by solution-precipitation cycles has given a powdery polymer, easily soluble at room temperature in aprotic polar

Tab. 1. Intrinsic viscosity values of poly(ABZAIA).

| Sample | $[\eta]^{25^\circ\text{C}}$ | $[\eta]^{50^\circ\text{C}}$ |
|-------------------|---------------------------------------|-----------------------------|
| | in 96% H ₂ SO ₄ | in DMF + 0.5 M LiCl |
| | dL · g ⁻¹ | dL · g ⁻¹ |
| V13 ^{a)} | 0.24 | 0.20 |
| V7 ^{a)} | 0.22 | 0.23 |
| MS1 ^{a)} | 0.29 | 0.31 |
| MS4 ^{a)} | 0.33 | 0.30 |
| MS5 ^{b)} | 0.40 | 0.39 |

^{a)} [TPP]/[COOH] = 1.09.

^{b)} [TPP]/[COOH] = 2.00.

solvents such as DMF, DMAc, NMP, and DMSO. By solvent evaporation from dilute solutions, a fragile, slightly coloured (pale yellow) film has been recovered.

The intrinsic viscosity data in sulfuric acid, compared to the $[\eta]$ values obtained at 50 °C by SEC-SCV (see below), are given in Tab. 1. Apart from obvious differences linked to the change of solvents (DMF + 0.5 M LiCl) and temperature (50 °C) in SEC measurements, the rather low values of intrinsic viscosity, together with the much better solubility of our HB polymer as compared to its linear analogue, are obviously linked to (and a direct proof of) the highly branched, compact polymer structure. In this respect, the knowledge of the polymer degree of branching (DB), as a function of both growth generations and experimental conditions of the synthesis, would be very helpful. At present, the synthesis of a model compound, which is a necessary pre-requisite for DB evaluation, is on the way and will be reported elsewhere^[24], together with DB values. Meanwhile, the above solution properties and SEC data already support a rather compact polymer shape, originated by the hyperbranched structure.

In Tab. 2, data obtained by SEC characterization are reported. MWDs are derived from two different configurations of the SEC apparatus (SEC-MALS and SEC-SCV). The discrepancy between them, in terms of \overline{M}_w values, goes from ca. 2 to ca. 18%, i.e. it is relatively small and does not appear linked to HB molecular weight, at variance with other systems.^[23] As expected, the polydispersity index $D = \overline{M}_w/\overline{M}_n$, evaluated by MALS, has been found substantially lower than the corresponding value obtained from SCV. Indeed, it is well known that MALS detector tends to underestimate the polydispersity, because of its poor sensitivity to low molecular weight fractions.^[23] Therefore, it is reasonable to consider the D ratios evaluated from the second configuration only, which provides values from ca. 2.7 to ca. 7.3, i.e. with a relatively large polydispersity. The last two columns of Tab. 2 give the $[\eta]$ values and the Mark-Houwink exponent a for the five poly(ABZAIA) samples. It is evident that a is changing from one sample to another and, generally, is an increasing function of molecular weight (except

Tab. 2. Summarized results of SEC-MALS-SCV characterization of the five poly(ABZAIA) samples.

| Sample | SEC-MALS | | SEC-SCV | | $[\eta]$ | a |
|--------|-----------------------|------|-----------------------|------|----------------------|------|
| | \overline{M}_w | D | \overline{M}_w | D | | |
| | g · mol ⁻¹ | | g · mol ⁻¹ | | dL · g ⁻¹ | |
| V13 | 87 050 | 2.19 | 80 650 | 2.67 | 0.19 ₈ | 0.15 |
| V7 | 55 500 | 2.19 | 65 650 | 4.16 | 0.23 ₃ | 0.29 |
| MS1 | 118 400 | 2.60 | 134 550 | 4.44 | 0.31 ₁ | 0.37 |
| MS4 | 85 300 | 1.90 | 83 800 | 3.65 | 0.29 ₇ | 0.32 |
| MS5 | 295 100 | 4.79 | 328 400 | 7.31 | 0.39 ₁ | 0.40 |

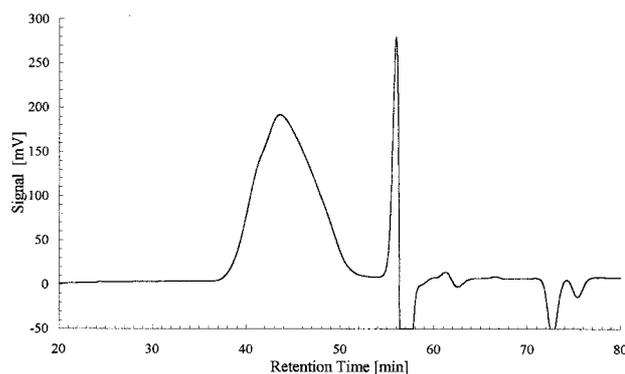


Fig. 2. Chromatographic trace of DRI detector for the V7 sample.

for V13). For the latter sample, an a value as low as 0.15 has been found, supporting a rather compact, close-to-globular shape. For the other four samples, however, a values increase (from 0.29 to 0.40) and suggest more open structures, presumably due to both different condensation pathways and a different number (and position) of unreacted functional groups, with preferential growth in some directions.

The former factor deserves a more detailed comment, so far as HB structures created by polycondensation (more precisely, by step polymerization) cannot be purely defined in terms of generations, being formed by random coupling of different n -mers. By definition, the resultant product is a complex mixture of geometrical isomers. Obviously, polydispersity is further implemented by differences in terms of molecular weights and degree of branching.

Fig. 2 shows the chromatographic DRI trace obtained with the V7 sample. The MWD curves for the five samples are shown in Fig. 3 (for the sake of simplicity, only those based on SEC-SCV are reported). It is evident that the shape of MWD curves, with the notable exception of the V7 sample, is supporting a bimodal character. However, a word of caution is necessary, as the aforementioned complexity aspects of the HB molecular architecture should always be kept in mind when D is evaluated by SEC.

On the basis of some recent findings^[11,12] for similar structures, liquid crystalline (LC) behaviour of poly(AB-

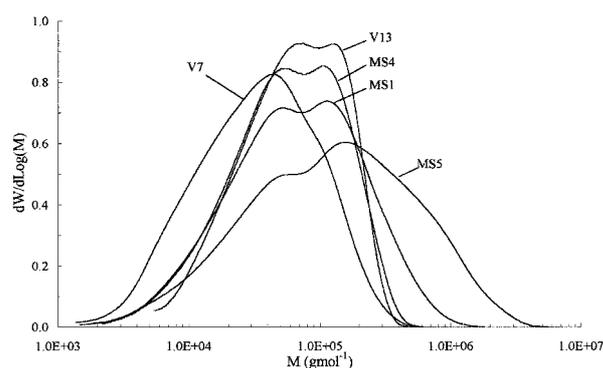


Fig. 3. Comparison of the differential MWD curves of five poly(ABZAIA) samples.



Fig. 4. Polarized light optical micrograph of a poly(ABZAIA) solution in NMP (60 wt.-%) under shear at room temperature.

ZAIA) has been checked. Indeed, as mentioned in the *Introduction*, Kim^[12, 14] already observed a lyotropic behaviour of some HB aramids synthesized in his laboratory and related the LC properties to the polymer propensity to form aggregates in neat amide solvents, as observed in SEC experiments.

In this respect, NMP solutions, containing increasing amounts of poly(ABZAIA), have been prepared. Starting from ca. 30 wt.-%, a shear birefringence under the polarizing microscope has been found at room temperature. Birefringence intensity increases by increasing polymer concentration. Fig. 4 shows a polarized light optical micrograph of a 60 wt.-% poly(ABZAIA) solution. The persistence of birefringence remains for a relatively long time, after shear stress has been removed. The persistence time is proportional to the polymer concentration and does not seem linked exclusively to viscosity increase.

Also for our system, polymer aggregation in solution has been observed by SEC, as quoted in a previous paper.^[15] In that ref. it has been reported that the apparent molecular weight of poly(ABZAIA) in neat DMF was ca. $2 \cdot 10^6$, while in DMF + 3 wt.-% LiCl it decreased to ca. $1 \cdot 10^5$. The salt seems to completely destroy the polymer

Tab. 3. Glass transition temperature of poly(ABZAIA) samples and onset of their thermal degradation.

| Sample | T_g °C | T_{onset} °C |
|--------|-------------|-------------------|
| V13 | 108 | 274 |
| V7 | 120 | 275 |
| MS1 | 144 | 275 |
| MS4 | 143 | 275 |
| MS5 | 139 | 274 |

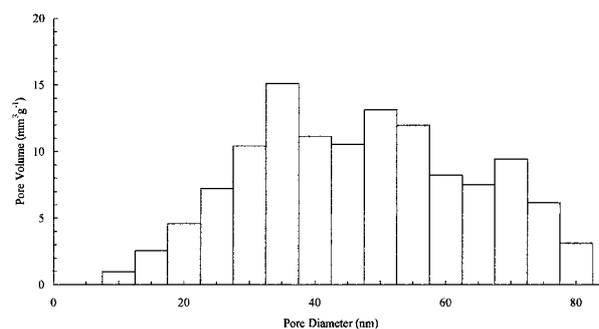


Fig. 5. Histogram of the pore size distribution as a function of pore diameter (sample MS1).

aggregation in solution. A detailed description of the LC behaviour of poly(ABZAIA) solutions will be given elsewhere.^[25]

Glass transition temperature of our samples is shown in Tab. 3, together with the onset of their thermal degradation (T_{onset}). As mentioned above, from the T_g data it is evident that, even when identical experimental conditions are applied to the poly(ABZAIA) synthesis, the reaction products are a statistical mixture not only in terms of molecular weights, but also as structural isomers with various DBs and geometrical shapes. This effect may explain the variation of the T_g values from one sample to another. In this respect, also SEC data should be considered only as a rough evaluation of molecular characteristics of our HB aramids and, in general, of any HB structure. The high values of T_{onset} confirm the excellent thermal stability of our HB aramids.

The powdered poly(ABZAIA) samples have been characterized in terms of surface area and pore size distribution, both relevant parameters to be known for potential industrial applications. Nitrogen adsorption/desorption isotherms at 77 K have been used in order to evaluate the above parameters. Our HB aramide samples show a specific surface area of ca. $30 \text{ m}^2 \cdot \text{g}^{-1}$, with an average pore diameter of 40 nm. A comparison with powdered poly(ϵ -caprolactam),^[26] which shows a specific surface area of ca. $2 \text{ m}^2 \cdot \text{g}^{-1}$, underlines the high porosity of our HB aramids.

The pore size distribution as a function of pore diameter (in nm) is shown in Fig. 5. The distribution is rela-

tively narrow, with a noteworthy fraction of pores below 30 nm. This high porosity, together with the excellent thermal stability and the surface which is very rich of functional groups, makes poly(ABZAIA) a potentially interesting material to be used, e. g. as a support for catalysts or biomolecules.

Conclusions and perspectives

A hyperbranched aromatic polyamide has been synthesized by direct condensation of 5-(4-aminobenzoylamino)isophthalic acid. The polymer, easily soluble in common organic solvents, shows good thermal stability and high porosity.

On one hand, the rather low Mark-Houwink a constant, calculated by SEC-SCV, confirms the hyperbranched, close-to globular shape of the polymer and on the other, with its variation from one sample to another, underlines the structural and shape complexity of our HB aramide. Highly concentrated polymer solutions in NMP show liquid crystalline behaviour at room temperature. Solid films from LC mesophases are in preparation and their properties will be compared to those of isotropic films.^[24, 25]

Acknowledgement: Financial support by MURST *Cofinanziamento '98* funds is acknowledged. The authors want to thank Dr. Marco Piacentini and Mr. Alberto Giacometti Schieronni for their valuable help in the synthesis of ABZAIA and poly(ABZAIA), and SEC evaluation, respectively. Prof. Estella Bianchi is gratefully acknowledged for helpful discussions on various aspects of the present work.

Received: January 20, 2000

Revised: June 12, 2000

[1] J. M. J. Fréchet, C. J. Hawker, "Synthesis and Properties of Dendrimers and Hyperbranched Polymers", in: *Comprehensive Polymer Science*, 2nd Suppl. Vol., S. Aggarwal, S. Russo, Eds., Pergamon, Oxford 1996, Ch. 3, p. 71 ff.

- [2] G. R. Newkome, C. N. Moorefield, F. Vögtle, "Dendritic Molecules – Concepts, Syntheses, Perspectives", VCH, Weinheim 1996.
- [3] Y. H. Kim, *J. Polym. Sci. Part A: Polym. Chem.* **1998**, *36*, 1685.
- [4] Y. H. Kim, O. W. Webster, *J. Am. Chem. Soc.* **1990**, *112*, 4592.
- [5] C. J. Hawker, R. Lee, J. M. Fréchet, *J. Am. Chem. Soc.* **1991**, *113*, 4583.
- [6] J. M. J. Fréchet, M. Henmi, I. Gitsov, S. Aoshima, M. Leduc, R. B. Grubbs, *Science* **1995**, *269*, 1080.
- [7] S. G. Gaynor, S. Edelman, K. Matyjaszewski, *Macromolecules* **1996**, *29*, 1979.
- [8] M. Suzuki, A. Ii, T. Saegusa, *Macromolecules* **1992**, *25*, 7071.
- [9] Y. H. Kim, O. W. Webster, *Macromolecules* **1992**, *25*, 5561.
- [10] A. Kumar, S. Ramakrishnan, *J. Chem. Soc., Chem. Commun.* **1993**, 1453.
- [11] R. Spindler, J. M. J. Fréchet, *Macromolecules* **1993**, *26*, 4809.
- [12] Y. H. Kim, *J. Am. Chem. Soc.* **1992**, *114*, 4947.
- [13] V. R. Reichert, L. J. Mathias, *Macromolecules* **1994**, *27*, 7024.
- [14] Y. H. Kim, *Macromol. Symp.* **1994**, *77*, 21.
- [15] S. Russo, A. Boulares, A. Mariani, *Macromol. Symp.* **1998**, *128*, 13.
- [16] G. Yang, M. Jikei, M. Kakimoto, *Macromolecules* **1998**, *31*, 5964.
- [17] G. Yang, M. Jikei, M. Kakimoto, *Macromolecules* **1999**, *32*, 2215.
- [18] S. Russo, A. Boulares, A. da Rin, A. Mariani, M.E. Cosulich, *Macromol. Symp.* **1999**, *143*, 309.
- [19] M. Jikei, S. Chon, M. Kakimoto, S. Kawauchi, T. Imase, J. Watanebe, *Macromolecules* **1999**, *32*, 2061.
- [20] M. E. Cosulich, S. Russo, S. Pasquale, A. Mariani, *Polymer* **2000**, *41*, 4951.
- [21] F. Higashi, S.-I. Ogata, Y. Aoki, *J. Polym. Sci., Part A: Polym. Chem.* **1982**, *20*, 2081.
- [22] A. Mariani, S. L. E. Mazzanti, S. Russo, *Can. J. Chem.* **1995**, *73*, 1960.
- [23] S. Russo, E. Bianchi, A. Congiu, A. Mariani, R. Mendichi, *Macromolecules* **2000**, *33*, 4390.
- [24] O. Monticelli, A. Mariani, S. Russo, manuscript in preparation.
- [25] O. Monticelli, D. Tabuani, E. Marsano, E. Bianchi, S. Russo, manuscript in preparation.
- [26] L. Ricco, O. Monticelli, S. Russo, manuscript in preparation.