Synthesis, characterisation and properties of aramid copolymers prepared from AB and AB$_2$ monomers

Orietta Monticelli[1] *, *Stefano Fiori*[2], *Alberto Mariani*[2], *Saverio Russo*[1], *Hartmut Komber*[3]

[1] Dipartimento di Chimica e Chimica Industriale, Università di Genova e unità di ricerca INSTM, via Dodecaneso 31, 16146 Genova, Italy; Fax +39 010 3536198; orietta@chimica.unige.it

[2] Dipartimento di Chimica, Università di Sassari e unità di ricerca INSTM, via Vienna 2, 07100 Sassari, Italy; Fax +39 079 229559; mariani@uniss.it

[3] Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany; Fax +49 351 4658565; komber@ipfdd.de

Abstract: Aromatic polyamide (aramid) copolymers having a highly branched architecture were prepared by direct polycondensation of an AB$_2$ monomer (5-(4-aminobenzoylamino)isophthalic acid) with an AB monomer (*N*-(4-aminophenyl)terephthalamic acid). Two synthetic routes have been followed for copolymer preparation, differing from each other in the overall monomer content and the type of salts added to the reaction medium (LiCl or LiCl + CaCl$_2$). Otherwise, both methods used the same conditions and the same condensing agent (triphenyl phosphite). The feed ratio of the monomers affected the copolymer solubility in aprotic polar solvents such as *N*,*N*-dimethylformamide, *N*-methylpyrrolidone and dimethyl sulfoxide. Only high AB$_2$/AB monomer ratios allowed obtaining completely soluble polymers in the above media. Also copolymer intrinsic viscosity was influenced by that ratio as well as by the polymerisation routes. IR measurements gave an indication of polymer structure evolution as a function of the monomer feed ratio, while ^{1}H NMR experiments verified the actual monomer composition in the synthesized polymers. The monomer feed ratio turned out to influence polymer properties, such as degree of crystallinity, thermal degradation temperature and liquid crystalline behaviour. Some of the characterisation techniques we used (^{1}H and ^{31}P NMR, IR, SEM-EDS) revealed the presence of phosphorus derivatives in the copolymers, despite extensive sample purification. This presence is coming from derivatives of the condensing agent, and is directly related to the content of AB$_2$-type structures present in the copolymers.

Introduction

Recently, the interest arisen from studies of hyperbranched (HB) polymers has been extended to their copolymers with linear monomers. Copolycondensation of AB$_2$ and AB monomers, already analyzed theoretically by Flory [1], was reconsidered by Kricheldorf *et al*. [2,3]. They reported the preparation of branched polymers by condensation of 3-(trimethylsiloxy)benzoyl chloride and 3,5-bis(trimethylsiloxy)-benzoyl chloride [2]. Later on, the same group studied the synthesis of branched

copolyesters with similar main chains but with different end groups [3]. Their attention was focused on the variation of branching extent by changing the feed ratio of difunctional to trifunctional monomers.

More recently Jikei *et al*. [4,5] studied the synthesis and properties of HB aramid copolymers prepared from AB (3-(4-aminophenoxy)benzoic acid) and AB_2 (3,5-bis(4-aminophenoxy)benzoic acid) monomers by direct polymerisation. Thermal properties (*i.e*., glass transition temperature and softening point) as well as mechanical properties turned out to be influenced by the monomer ratio.

A theoretical approach was followed by Litvinenko *et al*. [6,7], who analytically calculated the kinetics, as well as the average molecular weight and the average degree of branching for the self-condensing vinyl copolymerisation of a vinyl monomer with a molecule having a vinyl group and an initiating group (inimer). Besides polycondensation, other polymerisation methods (*e.g*., radical copolymerisation [8], cationic polymerisation [9], living anionic polymerisation [10], *etc*.) were used to prepare hyperbranched copolymers.

Solution rheology of a series of AB/AB_2 etherimide copolymers was studied by Markoski *et al*. [11,12]. It was found that the trend of viscosity was closely related to the distance between branches, suggesting the importance of this architectural parameter, which directly affects the properties of branched polymers.

In the present work, we report on the preparation of highly branched aromatic polyamides by copolycondensation of 5-(4-aminobenzoylamino)isophthalic acid (ABZAIA) with an AB monomer (*N*-(4-aminophenyl)terephthalamic acid) (APTA). The homopolymerisation of the AB_2 monomer leads to the formation of the HB polymer poly-(ABZAIA), extensively studied in previous works of ours [13-15] and characterised by a molecular structure, in terms of the sequence of CO and NH along the branches, similar to that of poly(*p*-benzamide) (PBA), while the AB monomer used in the present study is similar to the repeating unit of poly(*p*-phenyleneterephthalamide) (PPDT), both being linear aramids of relevant interest. The resultant copolymers combine the structure and the properties of the above linear homopolymers with those of a hyperbranched system. An accurate copolymer characterisation (in terms of solubility, intrinsic viscosity, thermal degradation behaviour, crystallinity) allowed to precisely determining the influence of monomer feed ratio on the properties of the resultant materials.

Experimental part

Materials

N-Methylpyrrolidone (NMP), Aldrich, was refluxed under reduced pressure in the presence of CaH_2 for 8 h and distilled under the same conditions. Then, it was refluxed under reduced pressure in the presence of P_2O_5 for 6 h and distilled; the treatment was repeated twice. Pyridine (Py), Aldrich, was refluxed under inert atmosphere in the presence of NaOH for 6 h and distilled; the treatment was repeated three times. LiCl, Carlo Erba, was dried for 24 h at 340°C in vacuum. Triphenyl phosphite (TPP), Aldrich, was purified by fractional distillation under reduced pressure for three times. LiCl, Carlo Erba, was dried for 24 h at 340°C in vacuum. Monomethyl terephthalate, thionyl chloride and anhydrous $CaCl_2$ (99.99%), all from Aldrich, were used as received.

Monomer synthesis

The trifunctional monomers, ABZAIA and ABAMIA (Fig. 1), were synthesized following the procedures given elsewhere [13-15].

ABZAIA monomer:

^{1}H NMR: δ = 13.2 (s, 2H, COOH), 10.09 (s, 1H, NH), 8.64 (d, 2H, H_{ar}), 8.15 (t, 1H, H_{ar}), 7.76 (d, 2H, H_{ar} *meta* to NH_2), 6.62 (d, 2H, H_{ar} *ortho* to NH_2), 5.79 (s, NH_2).

IR (KBr): broad absorption band from 3700 to 2500, 1660, 1563, 1511, 1590, 1422, 1393, 1331, 1286, 1247, 802, 766 cm^{-1}.

ABAMIA monomer:

^{1}H NMR: δ = 10.25 (s, 1H, NH), 8.70 (d, 2H, H_{ar}), 8.59 (t, 1H, H_{ar}), 7.39 (d, 2H, H_{ar} *meta* to NH_2), 6.56 (d, 2H, H_{ar} *ortho* to NH_2).

IR (KBr): broad absorption band from 3700 to 2000, 1712, 1619, 1512, 1394, 1331, 1241, 826, 740, 718, 679 cm^{-1}.

The difunctional monomer APTA (Fig. 1) was prepared following a procedure reported in ref. [16].
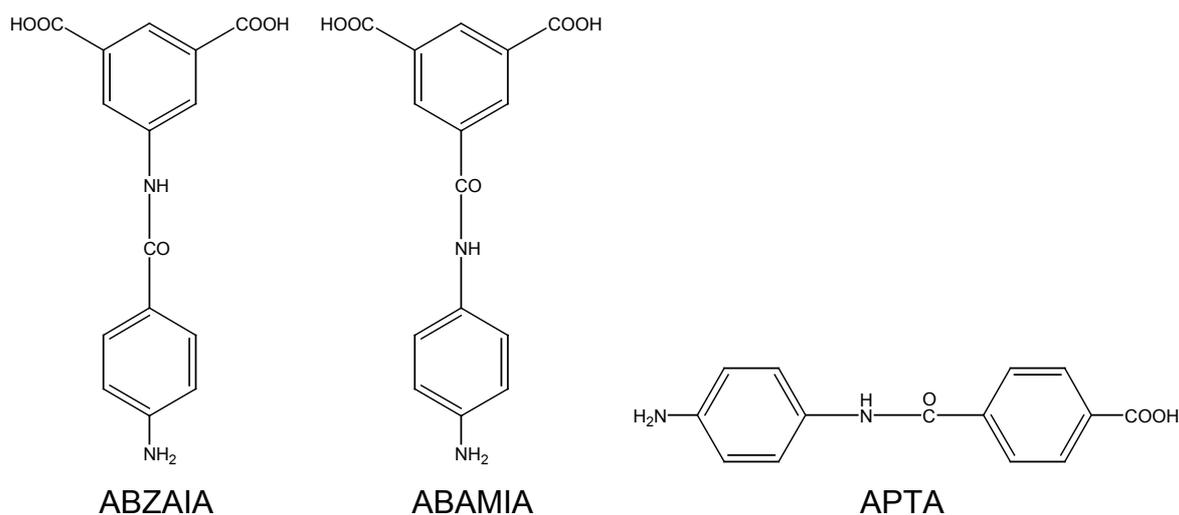

ABZAIA   ABAMIA   APTA

Fig. 1. Monomers

Synthesis of HB copolymers

As mentioned previously, two synthetic routes, named Yamazaki's and Higashi's method, respectively, were used for copolymer and homopolymer preparation. The former procedure, *i.e.*, the Yamazaki method, was described in previous works of ours for the synthesis of HB polymers from AB_2 monomers [13-15] as well as for those of PBA and low molecular weight PPDT [17]. AB_2 monomer concentration was 0.14 M in a 5:1 v/v mixture of NMP and Py, containing also 6.7 wt.-% LiCl; [TPP]/ [COOH] mole ratio was 1.1, polymerisation temperature (T_p) was settled at 115°C and polymerization time (t_p) at 4 h.

Higashi's method has been used previously for the synthesis of PBA and high molecular weight PPDT [17,18]. The procedure differs from the previous one in the monomer concentration and the salts added to the reaction medium. In fact, the

polymerization was carried out using a monomer concentration of 0.083 M in a solution containing 1.7 wt.-% LiCl and 5 wt.-% CaCl$_2$. The copolymer samples were collected by precipitation with methanol and washed in a Soxhlet with boiling methanol. Different copolymers were prepared varying the AB$_2$/AB mole ratio.

Characterization techniques

Solution viscosity was measured in a suspended level Ubbelohde viscometer at 25°C in 96% H$_2$SO$_4$.

Weight loss of samples as a function of temperature was determined by thermogravimetric analysis (TGA), in nitrogen atmosphere at a heating rate of 20°C/min, on a Perkin Elmer Thermal Analyzer Series 7.

TGA-FTIR measurements were carried out using a Pyris 1 TGA equipped with a TG-IR interface and a thermal analysis gas station (Spectrum GX). The same conditions as reported for the thermogravimetric analysis were employed.

Optical properties of poly(ABZAIA) solutions were investigated with a microscope Polivar Pol. Reichert Jung.

FTIR spectra were recorded with a Bruker IFS66 spectrometer on KBr pellets.

The degree of crystallization was evaluated via X-ray diffraction. Wide-angle X-ray scattering (WAXS) intensity profiles were collected with a Philips PW 1830 powder diffractometer (Ni-filtered Cu K$_\alpha$ radiation).

Phosphorus derivative concentration was measured via SEM-EDS analysis on a Leo Steroscan-440 scanning electron microscope, equipped with an EDS (energy dispersion spectroscopy) system (Oxford Link-Gem).

^{1}H and ^{31}P NMR spectra were recorded on a Bruker DRX 500 NMR spectrometer operating at 500.13 MHz for ^{1}H and at 202.45 MHz for ^{31}P. Dimethyl sulfoxide (DMSO-d_6) was used as solvent and internal standard ($\delta(^1$H$)$ = 2.50 ppm). The ^{31}P NMR spectra were referenced to external H$_3$PO$_4$ ($\delta(^{31}$P$)$ = 0 ppm).

Results and discussion

Copolymers were prepared varying the mole ratio of the monomers (ABZAIA and APTA) in the reaction medium, using both Yamazaki's and Higashi's methods. Tab. 1 (5th column) and Tab. 2 (3rd column) give the intrinsic viscosity data of the prepared copolymers and those of the linear and hyperbranched related polymers, poly(APTA) and poly(ABZAIA), respectively, for the two methods.

In order to test the reproducibility of the synthesis, some polymerisations have been doubled and are marked with (1) and (2). In the above tables the solubility data and the onset of their thermal degradation temperatures are also shown.

Examining the above tables, it appears evident that copolymer [η] strongly depends on both the monomer ratio AB$_2$/AB and the synthetic conditions used. Before discussing the results in detail, some preliminary considerations have to be drawn.

Tab. 1. Characterization of copolymers from ABZAIA/APTA prepared using Yamazaki's (Y) method

Entry	Sample code	AB$_2$ Monomer	AB$_2$/AB mole ratio	$[\eta]$ [a] in dL/g	Solubility in DMF, DMAc, DMSO, NMP	Solubility in H$_2$SO$_4$	Solubility in DMAc + 3 wt.-% LiCl	Solubilty in DMAc + 6 wt.-% LiCl	T_{onset} in °C
1	poly(APTA)Y(1)	ABZAIA	0/100	0.80	-	+	-	-	536
2	poly(APTA)Y(2)	ABZAIA	0/100	0.94	-	+	-	-	
3	ABZAPT9Y	ABZAIA	9/91	2.20	-	+	-	-	
4	ABZAPT25Y(1)	ABZAIA	25/75	3.25	-	+	-	-	448
5	ABZAPT25Y(2)	ABZAIA	25/75	3.00	-	+	-	-	
6	ABAMAPTA	ABAMIA	25/75	3.00	-	+	-	-	
7	ABZAPT50Y(1)	ABZAIA	50/50	0.85	-	+	-	-	
8	ABZAPT50Y(2)	ABZAIA	50/50	1.84	-	+	-	-	
9	ABZAPT75Y	ABZAIA	75/25	0.47	-	+	-	+	296
10	ABZAPT91Y	ABZAIA	91/9	0.34	+	+	+	+	267
11	poly(ABZAIA)Y	ABZAIA	100/0	0.35	+	+	+	+	270

[a] At 25°C; 96% H$_2$SO$_4$.

DMF: *N,N*-dimethylformamide; DMAc: *N,N*-dimethylacetamide; DMSO: dimethyl sulfoxide; NMP: *N*-methylpyrrolidone.

T_{onset}: Temperature of the onset of thermal degradation.

Tab. 2. Characterization of copolymers from ABZAIA/APTA prepared using Higashi's (H) method

Sample code	AB_2/AB mole ratio	$[\eta]$ [a] in dL/g	Solubility in DMF, DMAc, DMSO, NMP	Solubility in H_2SO_4	T_{onset} in °C
poly(APTA) [17]	0/100	4.3			
poly(APTA)H	0/100	8.40	-	+	572
ABZAPT25H	25/75	2.20	-	+	
ABZAPT50H	50/50	0.72	-	+	293
poly(ABZAIA)H	100/0	0.34	+	+	286

[a] At 25°C; 96% H_2SO_4.

First, the growth of a linear aramid structure is greatly influenced by the poor solubility of the macromolecule in the reaction medium while, owing to the much easier and higher solubility of the HB structure, hyperbranched polymer formation is less affected by the solvent power of the reaction medium. In this respect, Higashi's method, which involves the use of LiCl and $CaCl_2$ and lower monomer concentration, has a better solvent power and thus favours the formation of a linear aramid characterised by higher viscosity (8.40 dL/g) (Tab. 2). On the contrary, polymers prepared using Yamazaki's procedure exhibit lower viscosity (Tab. 1).

The sample poly(APTA)H deserves a more detailed comment as it holds an intrinsic viscosity value much higher than that reported by Preston *et al.* [19], although the same monomer and the same synthetic method were used. The discrepancy might be due to the different purification level for all reagents and solvent medium components reached in the two laboratories because, as described in a previous work of ours [17], the above reaction parameter plays an important role on both polyamidation kinetics and polymer molar masses. Detailed comments of this specific result are the subject of a forthcoming paper [16].

As far as Yamazaki's method is concerned, it is reasonable that, by increasing the ratio AB_2/AB, the polymer, which is more branched and consequently more soluble in the reaction medium, can grow further forming longer chains. This phenomenon can explain the peculiar trend (Fig. 2, open points), with a $[\eta]$ maximum *vs.* AB_2 content derived by two opposite effects: increased solubility and more compact shape of the copolymer chain. Conversely, Higashi's conditions, which are the most favourable for the growth of linear chains, show (full points) a regular, monotonic decrease of $[\eta]$ when increasing the AB_2 monomer content.

For both methods, by further increasing of the concentration of AB_2 monomer, the polymer viscosity decreases, mainly as a consequence of the formation of a highly branched quasi-globular structure. It is remarkable that the two curves initially cross over and finally super-impose each other. In other words, Higashi's conditions are better than Yamazaki's at low AB_2 content (< *c.* 15%) and less favourable in the region from 15 to *c.* 50%. Differences become negligible at higher AB_2 concentrations up to the neat poly(ABZAIA): $[\eta]$ = 0.35 dL/g by Yamazaki's method, 0.34 dL/g by Higashi's recipe, thus confirming that both solvent media have similar solvent power for these highly branched structures.
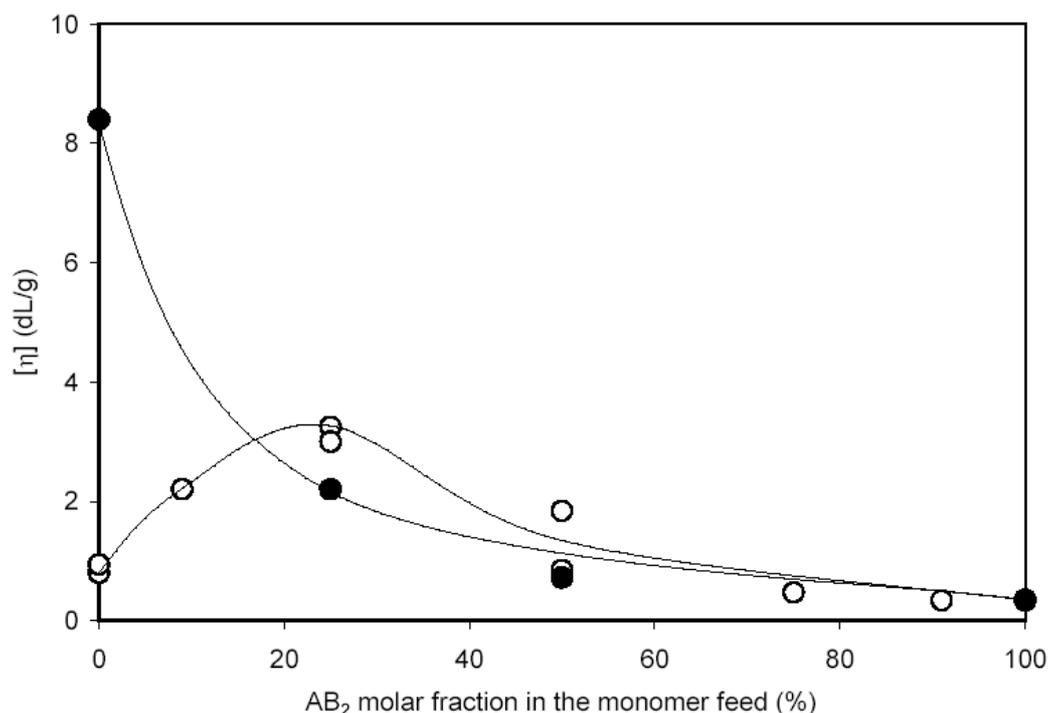
Fig. 2. [η] as a function of the trifunctional monomer mole fraction in the monomer feed (○ samples prepared via Yamazaki's method, ● samples prepared via Higashi's method)

In order to prove the influence of the specific AB_2 monomer structure on the co-polymer properties, another AB_2 monomer named ABAMIA, which holds NH and CO groups in an inverted central position with respect to ABZAIA, has been used (Fig. 1b). As far as linear polymers are concerned (*e.g.*, PPDT *vs.* PBA), a similar difference in the sequence of CO and NH leads to materials characterised by rather different properties (viscosity, solubility, mechanical properties, *etc.*). As shown in Tab. 1 (entry 6 *vs.* 5) copolymer features such as intrinsic viscosity and solubility do not seem to be influenced by the use of either comonomer.

All samples have been found soluble in H_2SO_4, while solubility in organic solvents (DMF, DMAc, DMSO, and NMP) was dependent on copolymer composition. Only at AB_2 content > 90% good solubility was found. Namely, sample ABZAPT91Y (entry 10, Tab. 1), prepared with the highest AB_2/AB monomer ratio (91/9), was completely soluble in all organic solvents of the list, analogously to the neat HB polymers poly-(ABZAIA)Y and poly(ABZAIA)H. This finding, together with the low [η] value, is a proof of copolymer structure evolution, which, when increasing the concentration of AB_2 monomer, goes from a linear to a highly branched one. The latter architecture, characterised by a large number of functional end groups and a close-to-globular three-dimensional structure, determines peculiar material properties.

As already reported [20], the presence of some specific salts in the solvent medium greatly improves polymer solubility. We have found that the sample ABZAPT75Y, insoluble in neat DMAc, becomes completely soluble in a DMAc solution containing 6 wt.-% LiCl. Thus, we have proved the possibility to prepare a sample, characterized by an intermediate structure between a linear and a HB aramid, which keeps the properties of a completely hyperbranched polymer (*i.e.*, low viscosity and high solubility).

Copolymer structural investigation

Copolymer samples obtained from different monomer ratios were characterised by FTIR. As most of the synthesised copolymers were insoluble in organic solvents, it was not possible to prepare their films on NaCl window; KBr pellets were used and the spectra show some scattering. As an example, spectra recorded for the homopolymers, poly(APTA)Y(1) and poly(ABZAIA)Y, and for the copolymer ABZAPT75Y are shown in Fig. 3.
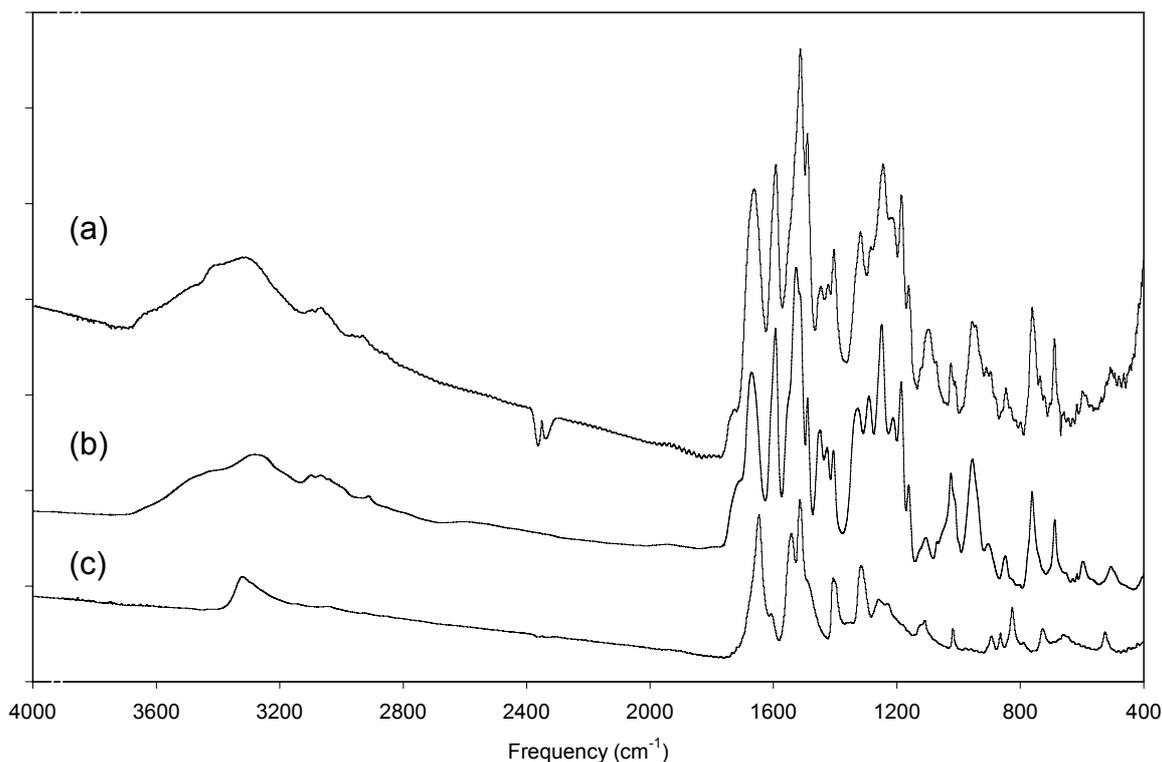

Fig. 3. FT-IR spectra of (a) the copolymer ABZAPT75Y, (b) the homopolymer poly(ABZAIA)Y, and (c) the homopolymer poly(APTA)Y(1)

The linear polymer poly(APTA)Y(1) shows absorption maxima at 3320 (N-H), 1646 (C=O amide), 1540 (ring band) and 1513 cm^{-1} (CNH). In the region below 1400 cm^{-1} several skeletal absorption bands are present: 1405 (*para*-substituted benzene), 1315 (CNH and ring bands), 1258 (C-O), 825 cm^{-1} (*para*-substituted benzene). By comparing its IR spectrum to that of the hyperbranched polymer poly(ABZAIA)Y, a significant difference in the region between 3500 and 2000 cm^{-1} occurs and is caused by absorption bands attributed to terminal groups NH_2 and COOH. Indeed, going from the linear to the HB structure, the number of end groups greatly increases while the CO$\cdots$HN interactions decrease. Furthermore, in the spectrum of the sample poly(ABZAIA)Y, new absorption bands are found at 1450 and 1280 cm^{-1}, together with a strong absorption at 956 cm^{-1}. These bands seem to be related to the branched structure as their intensity increases by increasing the monomer feed ratio AB_2/AB. The spectrum of the copolymer ABZAPT75Y, despite its intermediate composition, turns out to be very close to that of the sample poly(ABZAIA)Y.

As will be demonstrated further on in detail, it is possible to hypothesize that the above absorption maxima are caused by the presence of phosphorus derivatives entrapped in the polymeric structure, coming from the triphenyl phosphite used in the

8

synthesis as the condensing agent. In fact, the band at 1280 cm^{-1} is characteristic of the C-O bond of a phenoxy group, while that at 956 cm^{-1} is a peculiar band of penta-valent phosphorus compounds linked to P-O stretching.

In order to prove the presence of phosphorus in the synthesized samples and to verify its occurrence in relation to the polymeric structure, SEM-EDS measurements were carried out. In Fig. 4 phosphorus concentration is reported as a function of AB$_2$ concentration in the monomer feed. It appears evident that the entrapped amount of this element, which is relatively low for the linear aramid, sharply increases in the branched copolymers and reaches its maximum for an AB$_2$-unit content $> 75\%$.
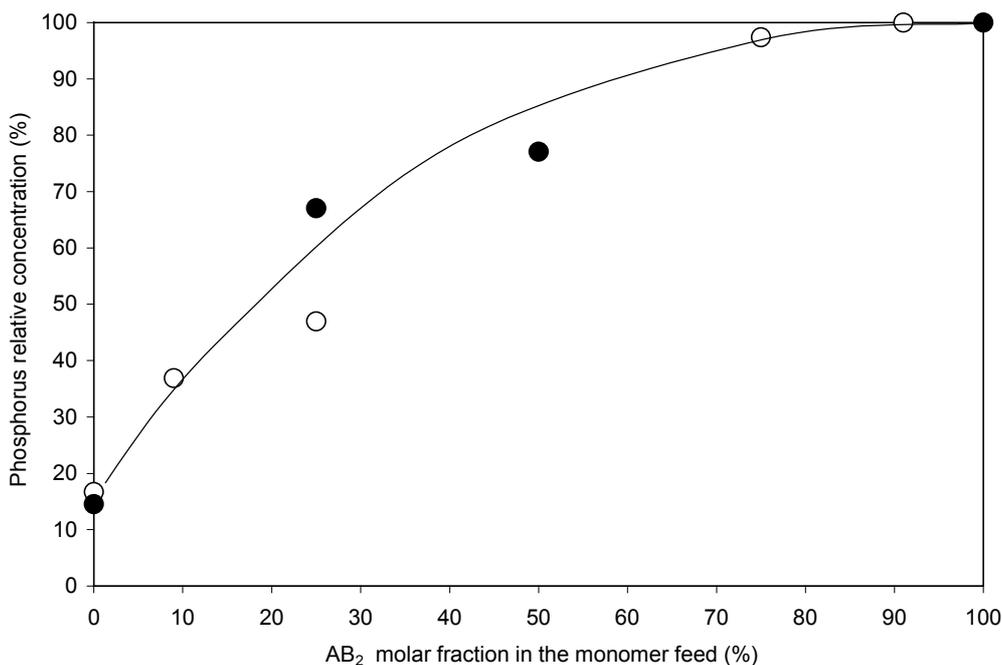
Fig. 4. Phosphorus concentration as a function of the AB$_2$ mole fraction in the monomer feed (○ samples prepared using Yamazaki's method, ● samples prepared using Higashi's method)

As all samples were purified following the same procedure, the above finding demonstrates the very difficult removal of phosphorus compounds from the dense and *quasi*-globular highly branched structure, also characterised by a high concentration of terminal groups.

Besides FTIR characterisation, the structure of our copolymers has been studied by ^{1}H NMR. In previous works [21,22] we proved the possibility to exploit the NMR technique in order to characterise in detail the fine structure of HB polymers prepared either from an AB$_2$ monomer (ABAMIA) or from A$_2$ (*p*-phenylenediamine) + B$_3$ (trimesic acid) reactants.

In contrast to those HB polymers, more complex spectra are expected for poly-(ABZAIA) due to the different substitution patterns of the 1,3,5-trisubstituted benzene (two C=O and one NH group) and the 1,4-disubstituted unit (one C=O and one NH group). In fact, several signals can be observed in the relevant chemical shift region between 7.7 and 9 ppm. Unfortunately, an assignment to positions 1 (1',1'') to 4 (4') in the linear (L), dendritic (D), and terminal (T) units of poly(ABZAIA) (Fig. 5) was not possible.
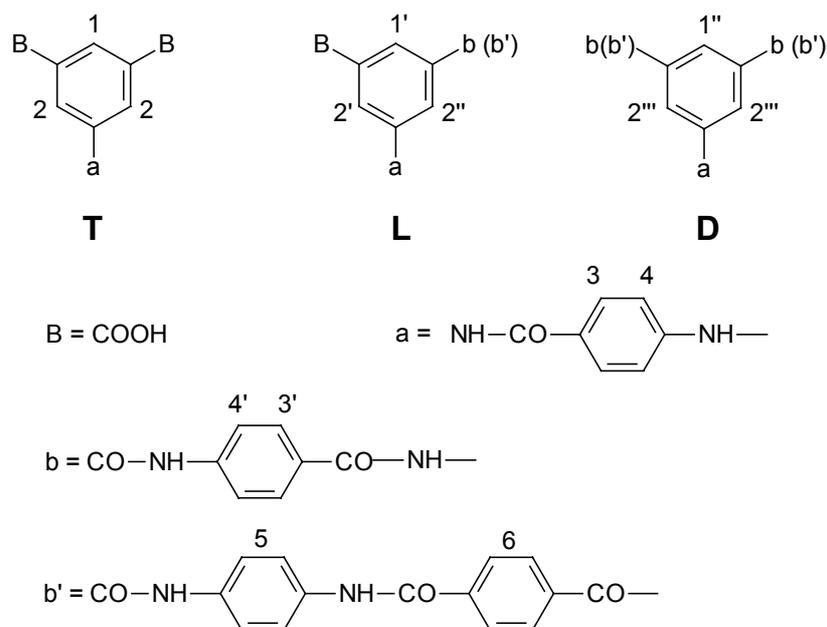
9

Fig. 5. Structural units of poly(ABZAIA) and copolymers

After the insertion of comonomer AB in the HB polymer structure, it is necessary to consider also the b' unit. Because the signals of protons 5 of this unit at 7.81 ppm are not overlapped by other signals, the content of the bifunctional monomer (b' unit) incorporated in the polymer can be calculated assuming that all signals between 7.9 and 9 ppm are caused by the remaining aromatic protons of the polymer.

We have focused our attention on two samples soluble in DMSO: the hyperbranched polymer poly(ABZAIA)Y and the copolymer ABZAPT91Y, prepared from the AB_2/AB feed ratio 91/9. ^{1}H NMR spectra of the aforementioned polymers are shown in Fig. 6. The AB_2/AB monomer ratio of sample ABZAPT91Y, calculated from its ^{1}H NMR spectrum, was found to be 88/12, a value very close to the feed ratio of the monomers.

Analyzing the entire spectra of the above samples, it is possible to identify signals in the region between 7.6 and 6.9 ppm, which do not belong to the polymers themselves. As already mentioned, these signals can be attributed to the presence of phosphorus derivatives. ^{31}P NMR measurements allowed studying the nature of these compounds. The sample poly(ABZAIA)Y gave the spectrum shown in Fig. 7.

The signals appear in two spectral regions: at about 11 ppm (X,X') and at about -11 ppm (Y,Y'). Neither the condensing agent TPP nor diphenyl phosphite, which is a coproduct of the direct polyamidation reaction [23], causes these signals. A one-bond P-H coupling could not be observed. From a ^{31}P,^{31}P COSY spectrum it could be proved that one compound contains two different phosphorus moieties (X',Y'; J_{PP} = 40 Hz). By comparison with literature data [24], we incline to assign the B/B' region to a $HOP(O)(OPh)(OR)$ or $HOP^+(OPh)_2(OR)$ structure with R = Ph for Y and R = P-containing X' for Y'. Signals in region X/X' may be caused by phosphonic acid ester structures formed by a P-O-Ph to P(O)Ph rearrangement. However, a clear structural identification for X, X'Y', and Y was not possible due to their low concentration and inclusion in the polymer. Nevertheless, we believe that charged sites and/or acidic groups resulting in ionic interactions with the polymers are the reason for the strong inclusion of these P-compounds in the polymer.
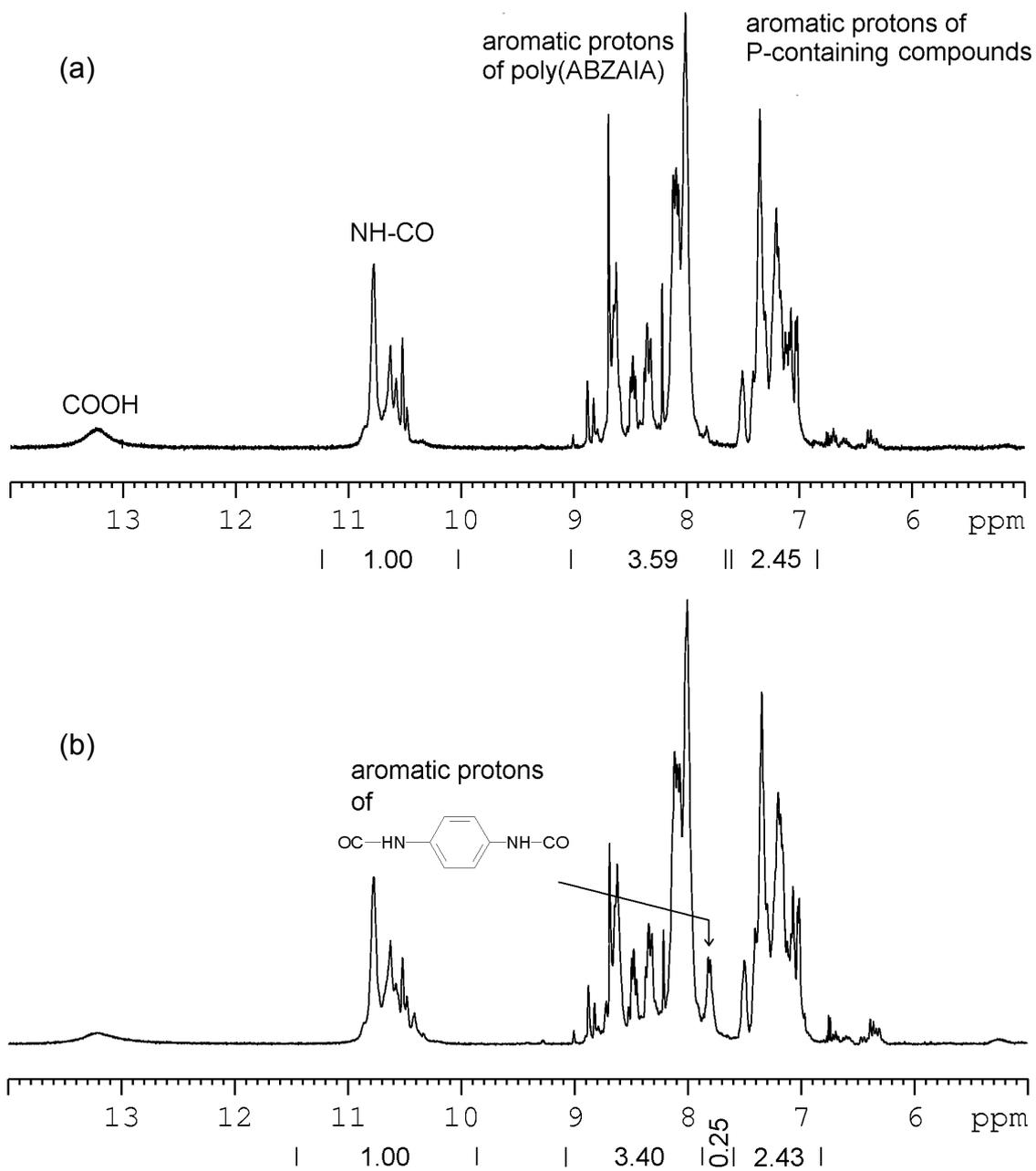
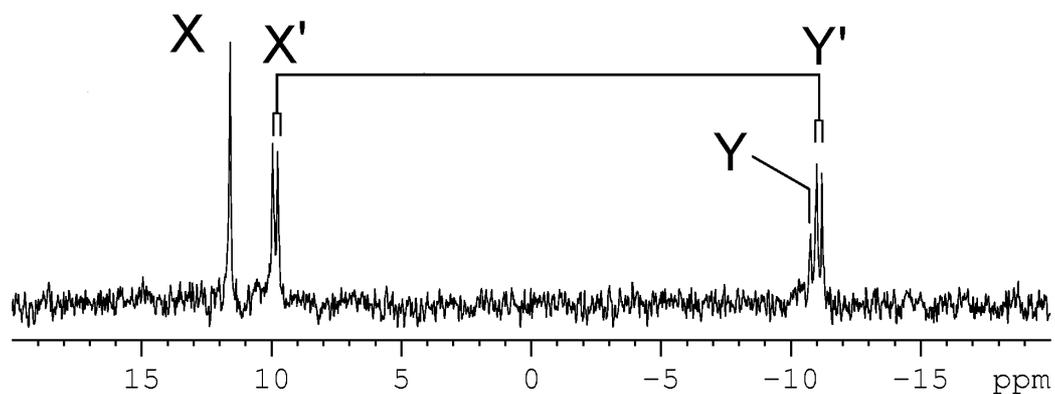Fig. 6. ^{1}H NMR spectra of (a) poly(ABZAIA)Y and (b) ABZAPT91Y

Fig. 7. ^{31}P NMR spectrum of poly(ABZAIA)Y

Copolymer crystallinity

Most of the hyperbranched polymers reported in literature are amorphous, although the linear analogous are known as crystalline polymers [25]. As far as our systems are concerned, linear PPDT-type polymers are highly crystalline, whereas HB aramids having a molecular structure similar to that of PPDT were found to be completely amorphous. On this basis, it is relevant to study the influence of the trifunctional/difunctional monomer ratio on copolymer crystallinity.

The degree of crystallinity, x_c, evaluated with the WAXS technique, is given by:

$$x_c(\%) = \frac{A_c}{A_c + A_a} \times 100$$

where A_a is the area due to amorphous diffusion and A_c is the area of the crystalline peak.

As an example, the spectra of four samples (poly(APTA)Y(1), ABZAPT9Y, ABZAPT25Y(1), ABZAPT50Y) are shown in Fig. 8. Linear homopolymers and copolymers, both prepared using Higashi's method, are characterised by similar spectra.
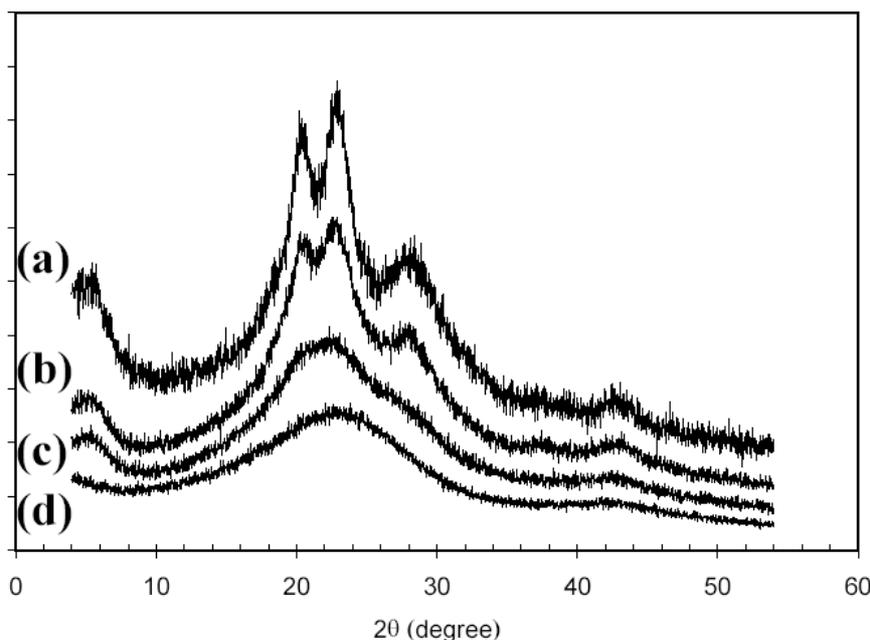
Fig. 8. WAXS intensity profiles of the samples: (a) poly(APTA)Y(1), (b) ABZAPT9Y, (c) ABZAPT25Y(1), (d) ABZAPT50Y

The WAXS intensity profile of the sample ABZAPT50Y, completely amorphous, has been used to draw the amorphous halo. x_c values of several copolymers and homopolymers, calculated from the equation given above, are listed in Tab. 3.

As predictable from the change of the polymeric structure, a higher content of AB_2 co-monomer in the monomer feed leads to the formation of increasingly amorphous copolymers. However, it is interesting to point out the possibility to obtain copolymers characterised by a partially branched structure and not completely amorphous.

Furthermore, the use of different synthetic methods seems to influence not only [η], but also the crystallinity of the resultant homopolymer. Indeed, compared to

Yamazaki's method, Higashi's conditions lead to the formation of more crystalline poly(APTA) (*c*. 24% *vs*. 18%).

Tab. 3. Degree of crystallinity of copolymers ABZAIA/APTA and the parent homo-polymers prepared using Yamazaki's (Y) and Higashi's (H) conditions

Sample code	AB_2/AB	x_c in %
poly(APTA)Y(1)	0/100	18.4
ABZAPT9Y	9/91	15.8
ABZAPT25Y(1)	25/75	4.8
ABZAPT50Y(1)	50/50	0
poly(APTA)H	0/100	24.2
ABZAPT25H	25/75	4.0
ABZAPT50H	50/50	0

Polymer thermal properties

Together with the aforementioned properties, also polymer thermal stability is greatly influenced by the monomer feed ratio (Tabs. 1 and 2, last column). While linear aramids are characterised by a high thermal stability, T_{onset} of the copolymers is sharply reduced by increasing AB_2 concentration in the feed ratio. The degradation temperature, which is higher than 500°C for the linear homopolymers, goes down to a plateau around 280°C for the copolymers. In addition to straightforward consider-ations on the stability of linear structures *vs*. branched ones, it is also important to point out that this property may be strongly affected by impurities, as phosphorus derivatives that, as described above, come from the synthesis itself and are firmly entrapped in the highly branched polymer matrix.

Thermogravimetric analysis combined with FTIR measurements allowed supporting the above hypothesis. Fig. 9 (a and b) shows the thermogravimetric (TG) and the corresponding derivative (DTG) curves, respectively, of the homopolymers poly-(APTA)H and poly(ABZAIA)H. The thermal behaviour of the two samples is completely different. While the linear polymer decomposes in a single step at high temperature, the weight loss process of the HB aramid occurs in three steps, as can be seen from the three minima in the DTG curves (Fig. 9b).

As shown in Fig. 10, FTIR spectra of the gases evolved from the two polymers at high temperature (above 500°C) are similar. Absorption maxima, present at 2340, 2308, 2164, 2086 and 1498 cm^{-1}, can be related to ammonia and carbon dioxide formation due to polymer decomposition. At lower temperature (256°C) the resultant spectrum of gases evolved by the hyperbranched polymer shows an absorption band at 1730 cm^{-1}, which corresponds to the first decomposition step (from 180 to 330°C) (Fig. 11). The interpretation of the spectrum needs additional work and is, at present, under detailed investigation. Nevertheless, the above absorption band does not seem to be related to polymer decomposition. As the other characterisation techniques (NMR, SEM-EDS) revealed only impurities of phosphorus derivatives in the polymeric matrix, we can assume that the first thermal decomposition is due to these compounds.
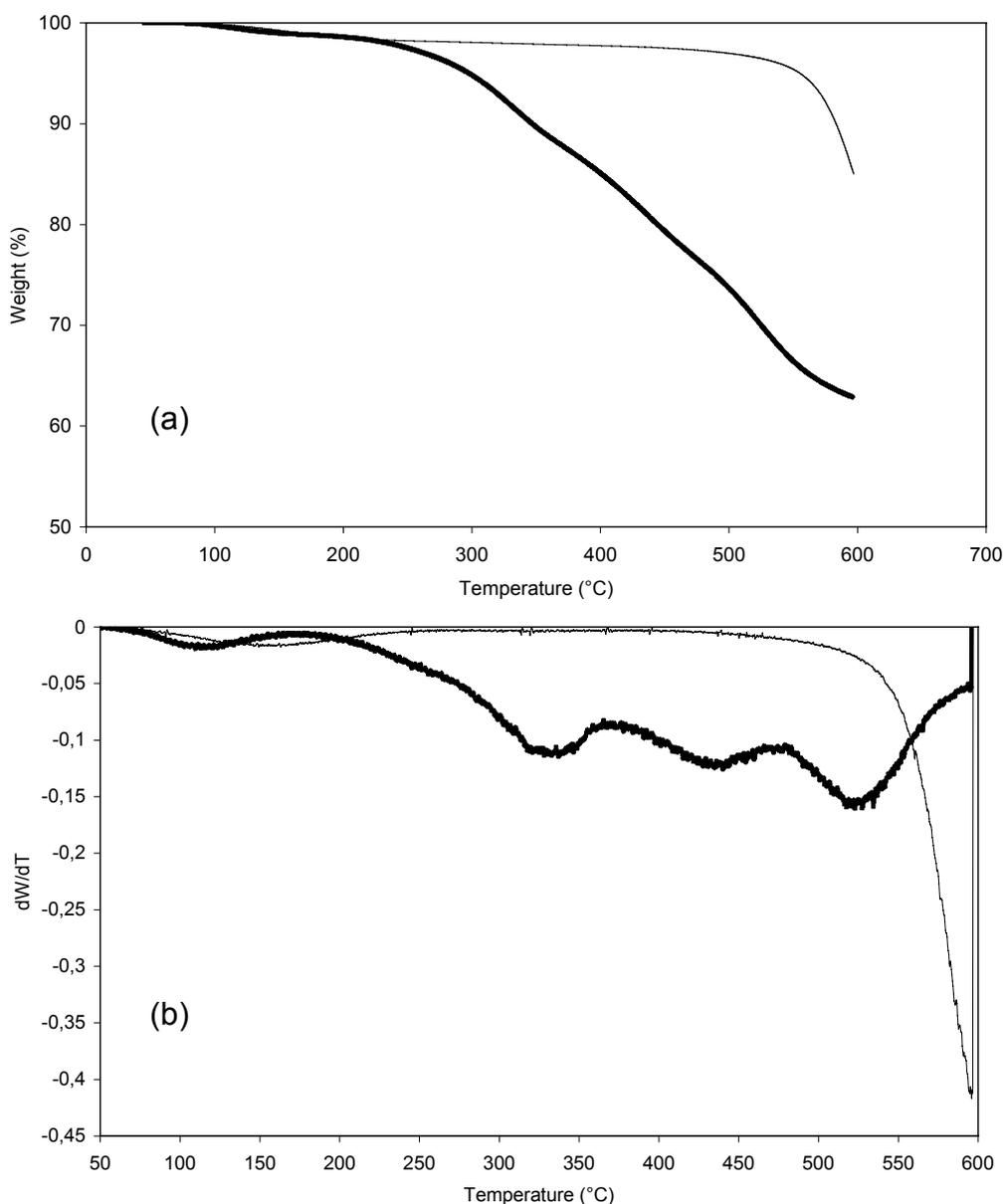
Fig. 9. (a) TG curves of poly(APTA)H and poly(ABZAIA)H; (b) DTG curves of poly(APTA)H and poly(ABZAIA)H

LC polymer properties

One of the most interesting features of HB aramids is the liquid crystalline (LC) behaviour of their concentrated solutions in organic solvent, such as DMF, DMAc, DMSO. This property, first observed by Kim [26], was found also for other hyper-branched structures, including our HB polyamides prepared from AB_2 monomers [15] and $A_2 + B_3$ reactants [21]. The LC behaviour, not yet fully clarified, was related to the tendency of the polymers to form aggregates in solution. It is worth mentioning here that the above structures give also rise to thermotropic LC films.

In order to study the influence of the polymeric structure on this property, DMSO solutions of two soluble polymers (the hyperbranched polymer poly(ABZAIA)Y and the copolymer ABZAPT91Y) were prepared. It was noticed that the concentration, at which shear birefringence starts, changes for the two systems. While the HB polymer holds a critical concentration (C'_p) at about 35 wt.-%, the solution of the copolymer

14

becomes already birefringent at about 20 wt.-% (Fig. 12). This finding underlines that the critical concentration is linked to the monomer feed ratio, which is responsible for the resultant polymer structure. Indeed, a more linear and open structure seems to facilitate the polymer self-assembly in solution.
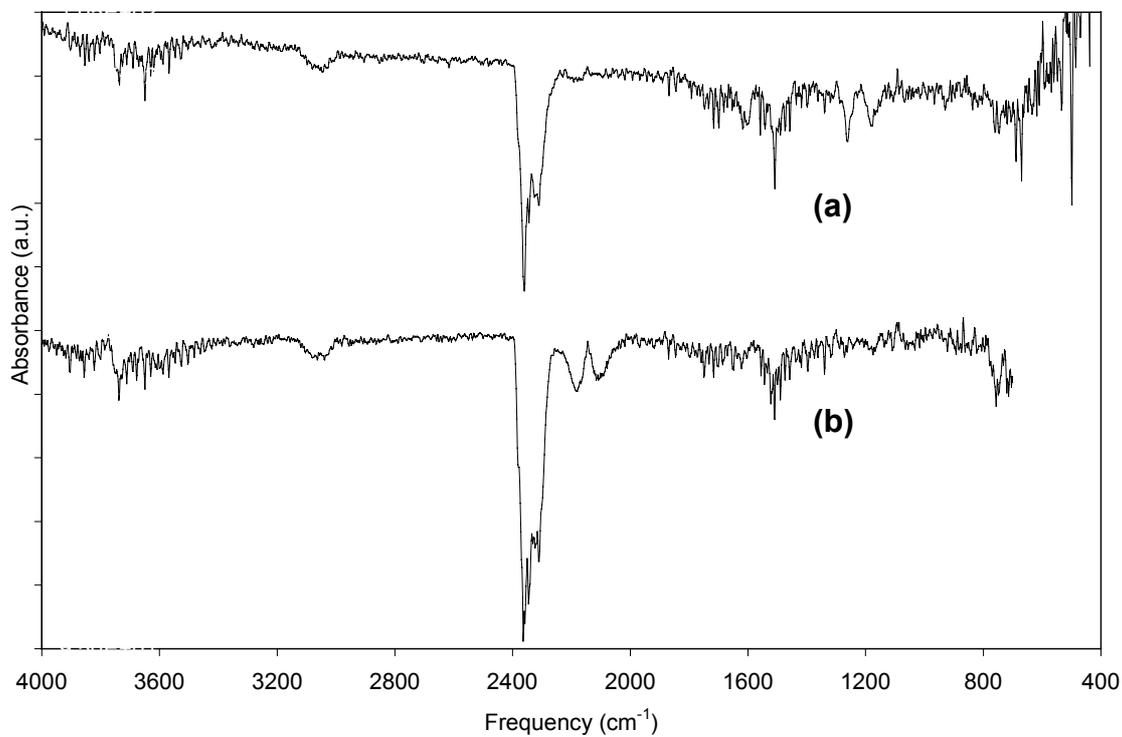
Fig. 10. FT-IR spectrum of gas evolved (a) from poly(ABZAIA)H at 520°C, and (b) from poly(APTA)H at 600°C
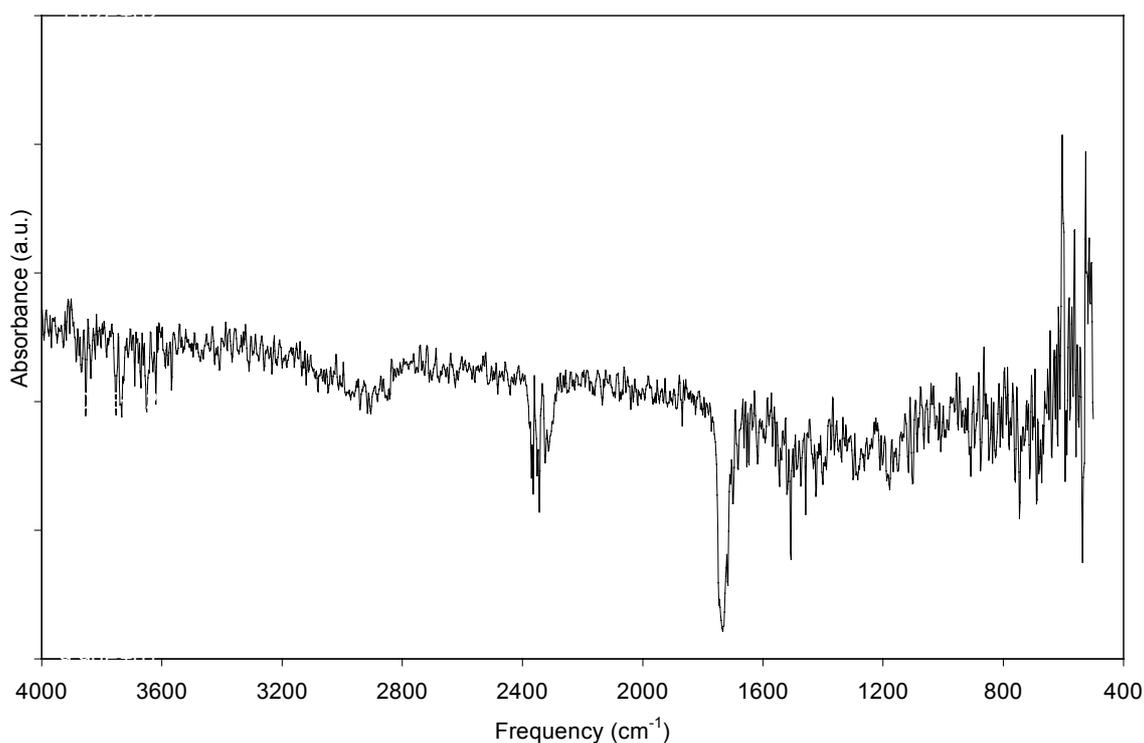
Fig. 11. FT-IR spectrum of gas evolved from poly(ABZAIA)H at 256°C
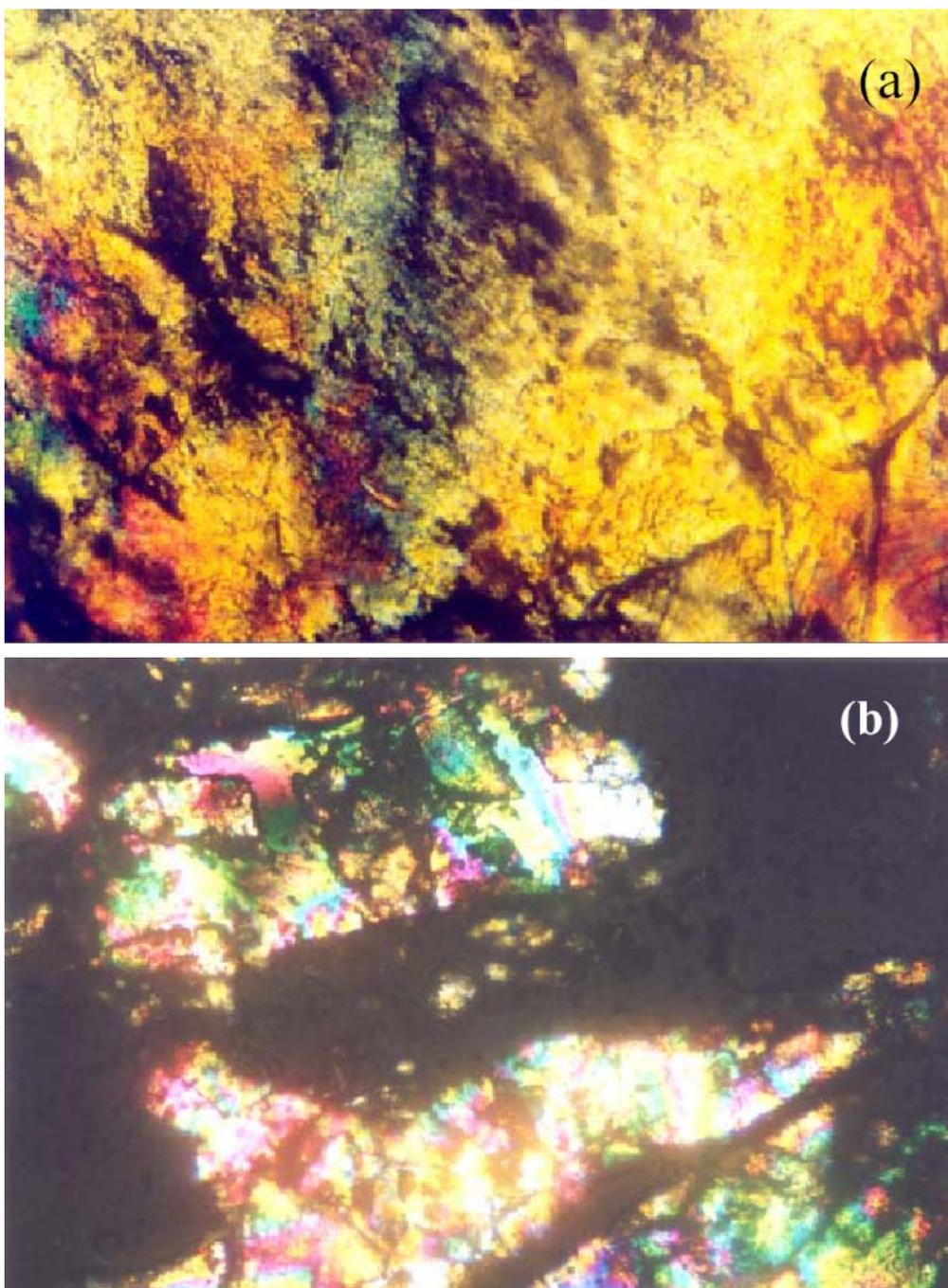
Fig. 12. Polarized light optical micrographs of (a) poly(ABZAIA)Y solution in DMSO (50 wt.-%) under shear at room temperature, and (b) ABZAPT91Y solution in DMSO (30 wt.-%) under shear at room temperature

A word of caution is, however, necessary, as birefringence in itself is not a sure proof of LC character, and additional experiments are necessary. However, analogies with previous HB aramid structures synthesized by us may justify the above speculation. Indeed, in that reference fully reversible thermotropic behaviour after repeated temperature cycles seems to strongly support true LC characteristics. At the same time, it has been demonstrated that the polymer properties in solution such as viscosity and solubility can be easily and finely tuned by changing the reaction parameters and the monomer feed ratio AB_2/AB.

Conclusions

Aramid copolymers were synthesized by direct polycondensation of (5-(4-amino-benzoylamino)isophthalic acid and *N*-(4-aminophenyl)terephthalamic acid, *i.e.*, an AB_2 and AB monomer, following two synthetic methods. The linear polymer properties (solution viscosity, cristallinity, thermal degradation temperature) turned out to depend on the synthetic methods used and were influenced by the monomer feed ratio. Furthermore, the viscosity of copolymers characterised by a low AB_2/AB monomer ratio and prepared by the two synthetic routes followed different trends. Preliminary results pointed out the possibility to influence also the anisotropization concentration by varying the monomer feed ratio.

Polymer characterisation demonstrated that phosphorus derivatives, coming from TPP, were not removed by extensive polymer purification and were largely concentrated in the hyperbranched structures. In particular, NMR studies revealed that strong ionic interactions took place between the polymer matrix and the P-containing compounds. The presence of the phosphorus derivatives could modify polymer properties such as the thermal degradation temperature. Our findings underline potential problems related to the use of this condensation agent in the preparation of hyperbranched polymers.

[1] Flory, P. J.; "*Principles of Polymer Chemistry*", Cornell University Press, Ithaca, New York **1953**.

[2] Kricheldorf, H. R.; Zang, Q.-Z.; Schwarz, C.; *Polymer* **1982**, *23*, 1821.

[3] Kricheldorf, H. R.; Stöber, O.; Lübbers, D.; *Macromol. Chem. Phys.* **1995**, *196*, 3549.

[4] Jikei, M.; Fujii, K.; Yang, G.; Kakimoto, M.; *Macromolecules* **2000**, *33*, 6228.

[5] Fujii, K.; Jikei, M.; Kakimoto, M.; presented at *Polycondensation 2000*, Tokyo, September **2000**.

[6] Litvinenko, G. I.; Simon, P. F. W.; Müller, A. H. E.; *Macromolecules* **1999**, *32*, 2410.

[7] Litvinenko, G. I.; Simon, P. F. W.; Müller, A. H. E.; *Macromolecules* **2001**, *34*, 2418.

[8] Gaynor, S. G.; Edelman, S.; Matyjaszewski, K.; *Macromolecules* **1996**, *29*, 1079.

[9] Puskas, J. E.; Grasmüller, M.; *Macromol. Symp.* **1998**, *132*, 117.

[10] Ishizu, K.; Takeda, H.; Furukawa, T.; *Polymer* **2000**, *41*, 8299.

[11] Markoski, L. J.; Thompson, J. L.; Moore, J. S.; *Macromolecules* **2000**, *33*, 5315.

[12] Markoski, L. J.; Moore, J. S.; Sedijarevic, I.; McHugh, A. J.; *Macromolecules* **2001**, *34*, 2695.

[13] Russo, S.; Boulares, A.; Mariani, A.; *Macromol. Symp*. **1998**, *128*, 13.

[14] Russo, S.; Boulares, A.; Cosulich, M. E.; da Rin, A.; Mariani, A.; *Macromol. Symp*. **1999**, *143*, 309.

[15] Monticelli, O.; Mendichi, R.; Bisbano, S.; Mariani, A.; Russo, S.; *Macromol. Chem. Phys*. **2000**, *201*, 2123.

[16] Mariani, A.; Monticelli, O.; Fiori, S.; Russo, S.; submitted to *e-Polymers*.

[17] Mariani, A.; Mazzanti, S. L. E.; Russo, S.; *Can. J. Chem*. **1995**, *73*, 1960.

[18] Russo, S.; Mariani, A.; Ignatov, V. N.; Ponomarev, I. I.; *Macromolecules* **1993**, *26*, 4984.

[19] Preston, J.; Krigbaum, W. R.; Kotek, R.; *J. Polym. Sci., Polym. Chem. Ed*. **1984**, *22*, 873.

[20] Papkov, S. P.; Kulichikhin, V. G.; Kalmykova, V. D.; Malkin, A. Y.; *J. Polym. Sci., Polym. Phys. Ed*. **1974**, *44*, 1753.

[21] Monticelli, O.; Mariani, A.; Voit, B.; Komber, H.; Mendichi, R.; Pitto, V.; Tabuani, D.; Russo, S.; *High Perform. Polym.* **2001**, *13*, S45.

[22] Komber, H.; Voit, B.; Monticelli, O.; Russo, S.; *Macromolecules* **2001**, *34*, 5487.

[23] Lin, J.; Sherrington, D. C.; *Adv. Polym. Sci*. **1994**, *111*, 177.

[24] Berger, S.; Braun, S.; Kalinowski, H.-O.; "*NMR Spectroscopy of the Non-Metallic Elements*", John Wiley & Sons, Chichester **1997**.

[25] Kim, Y. H.; Webster, O.; *J. Macromol. Sci. - Polym. Reviews* **2002**, *C42*, 55.

[26] Kim, Y. H.; *J. Am. Chem. Soc*. **1992**, *114*, 21.