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Polymer 44 (2003) 7829–7841
polymer
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Structural modifications and fibre processing of hydroxy-functionalised mesogenic polyazomethines

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Received 3 January 2003; received in revised form 11 August 2003; accepted 9 October 2003

Abstract

A number of semiflexible homopolyazomethines and copolyazomethines based on hydroxy-functionalised mesogenic cores have been synthesised and characterised. The reported polymers include structural modifications such as an alteration of the coaxiality, shortening of the flexible spacers or copolymerisation to attain materials with reduced melting temperatures and suitable processability. These structural alterations have been introduced by condensing different α,ω-bis-[(4-formyl-3-hydroxyphenyl)oxy]alkanes with 2-methyl-1,4-phenylenediamine and/or 4-methyl-1,3-phenylenediamine. Fibres have been melt extruded from those nematic polyazomethines with the most favourable thermal properties. As-spun and tension-annealed fibres have been investigated by thermal analysis (TGA and DSC), X-ray diffraction and SEM microscopy in an attempt to infer a relationship between microstructure and tensile properties. From the results presented here, copolymerisation incorporating flexible spacers of different lengths seems to be the best strategy to balance ease of processing and tensile properties. Some of the fibres have improved mechanical properties compared with those previously reported for this class of semiflexible polyazomethine. A nematic polyazomethine with a decamethylenic spacer has also been modified with low percentages of several metal ions [Fe(III), Zn(II), V(IV) and Ni(II)] in order to establish a comparison with previously reported Cu(II)-modified fibres.

Keywords: Polyazomethines; Nematic fibres; Mechanical properties

1. Introduction

Initial reports described polyazomethines as insoluble and infusible polymers, a situation that would minimise their practical applications. However, different chemical modifications are available to reduce melting temperatures and to promote the appearance of specific properties such as mesomorphism [1]. The formation of liquid crystalline phases with changes in temperature is indeed a valuable phenomenon because the anisotropic properties of the materials in question are useful for a variety of applications. For instance, thermotropic liquid crystal polymers can be processed from the mesophase into high-performance fibres in which the exceptional tensile properties are a consequence of the parallel molecular alignment with the fibre axis [2].

Indeed, the preparation of thermotropic polyazomethines with moderate melting temperatures has been the goal of several studies published in this area. Pioneering work by DuPont showed that melting temperatures can be effectively reduced either by incorporating lateral substituents or flexible spacers into the polymeric chain, thus favouring the formation of mesophases [3–6]. This work by DuPont proved that fibres of wholly aromatic polyazomethines extruded from the anisotropic melt have better tensile properties than those of semiflexible polyazomethines, but that the incorporation of flexible spacers provides processing advantages. In any case, the tensile properties of the fibres can be substantially improved by thermal annealing.

For some time we have been investigating the properties of semiflexible polyazomethines. Several studies on the structure-property relationships in these polyazomethines have shown that the incorporation of a flexible spacer containing ten carbon atoms and the use of a suitable diamine comonomer can effectively decrease the melting temperature and promote liquid crystalline behaviour [7,8]. Some of these thermotropic polyazomethines have been

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0032-3861/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2003.10.032

melt-spun from their nematic melt into well-oriented high-strength fibres whose mechanical properties were improved by thermal treatments under tension carried out just above the glass transition temperature [9,10]. Thermal annealing under tension induces the development of crystallinity together with an improved molecular alignment along the fibre axis. These two factors, together with a gain in molecular weight, lead to increased tensile properties.

The most remarkable feature of the polyazomethines that we investigated was the incorporation of a hydroxyl group in the *ortho*-position of the Schiff base. It has been shown that hydroxy-functionalisation dramatically influences the physical properties of the polyazomethine and, therefore, the possibility of obtaining fibres with the desired mechanical properties [10]. Nevertheless, the presence of these functional groups allows the subsequent incorporation of low percentages of metal atoms whilst still retaining the liquid crystalline properties. The incorporation of paramagnetic metal centres, such as Cu(II), Fe(III) or V(IV), provides significant structural information when the metal-modified polymers are studied by electronic paramagnetic resonance [11,12]. Furthermore, polyazomethines modified with small amounts of Cu(II) ions, where the metal ion acts as a cross-linking site, can still be spun into fibres where the cohesive fibrillar interactions are considerably improved by the existence of covalent bonds [10,13].

Along with these studies, the main objective of this paper is to report novel structural modifications to this family of polyazomethines and investigate the influence of such changes on the tensile properties of the extruded fibres. In several of these materials such modifications have not been attempted to date. The homo- and copolyazomethines prepared in this work are shown in Fig. 1. Three strategies were employed to produce polymers with reduced processing temperatures: (i) modification of the length of the flexible spacer, (ii) alteration of the coaxiality in the mesogenic rigid core and (iii) copolymerisation. With these aims in mind, three dialdehydes containing 2, 6 or 10 carbon atoms in the spacer were condensed with a *para*- or a *meta*-substituted diamine to give different homopolyazomethines. The exclusive use of the *meta*-substituted diamine (which alters the colinearity) or dialdehydes with short spacers (which increase the melting temperatures) would preclude the formation of a mesophase. For this reason several copolyazomethines were also prepared.

The properties of polymer P10-p and its fibres have already been reported in previous papers [9,10]. In the present work, a fresh sample of polymer P10-p was synthesised and new fibres were extruded in order to make the data directly comparable. Therefore only newly obtained results are included in the discussion.

We also investigated the influence of metal complexation with different metals. In previous papers, modification of P10-p with 2% of Cu(II) was reported [10,13]. In an attempt to gain an understanding of the effect of metal complexation we have incorporated Zn(II), Ni(II), Fe(III), and V(IV) in the systems reported here (Fig. 2).

2. Experimental section

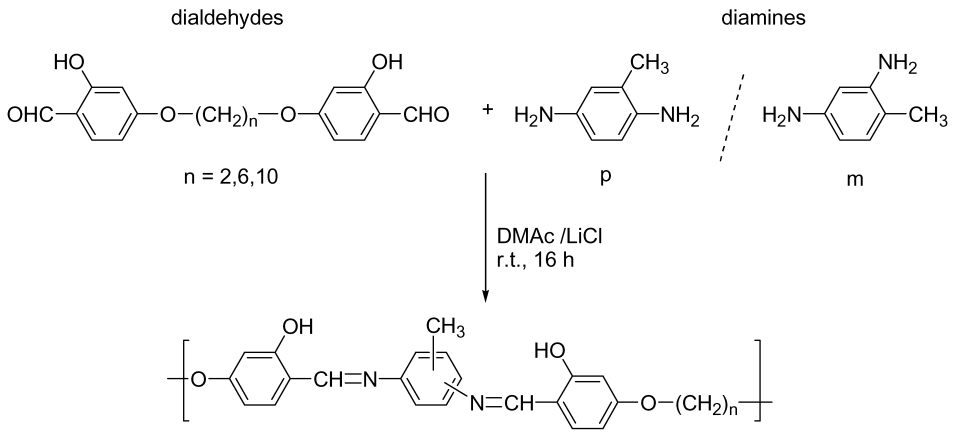
2.1. Monomers

Complex dialdehydes incorporating different alkyl segments were prepared according to a previous report [14]. 2-Methyl-1,4-phenylenediamine was obtained from its ammonium sulphate salt and purified immediately prior to use by vacuum distillation. 4-Methyl-1,3-phenylenediamine was commercially available and was distilled under vacuum prior to use.

2.2. Polymers

Polymerisation in solution was carried out in *N*,*N*-dimethylacetamide at room temperature as described in previous papers [9]. To a solution of LiCl (2.5 g) in *N*,*N*-dimethylacetamide (50 ml) under an inert atmosphere at room temperature was added the corresponding phenylenediamine (25 mmol). When the mixture became clear, the corresponding dialdehyde (25 mmol) was added. The solution was protected from light and stirred at room temperature for 16 h. Water was added to the resulting suspension and the yellow solid was isolated by filtration and thoroughly washed several times with water and methanol. The product was extracted (Soxhlet apparatus) with acetone for 24 h and finally dried under vacuum over P_2O_5 for 24 h at 80 °C to give the polyazomethine. IR, ^{1}H NMR and elemental analyses were in accordance with the proposed structures. Polymerisation yields and relevant characterisation data are collected in Table 1.

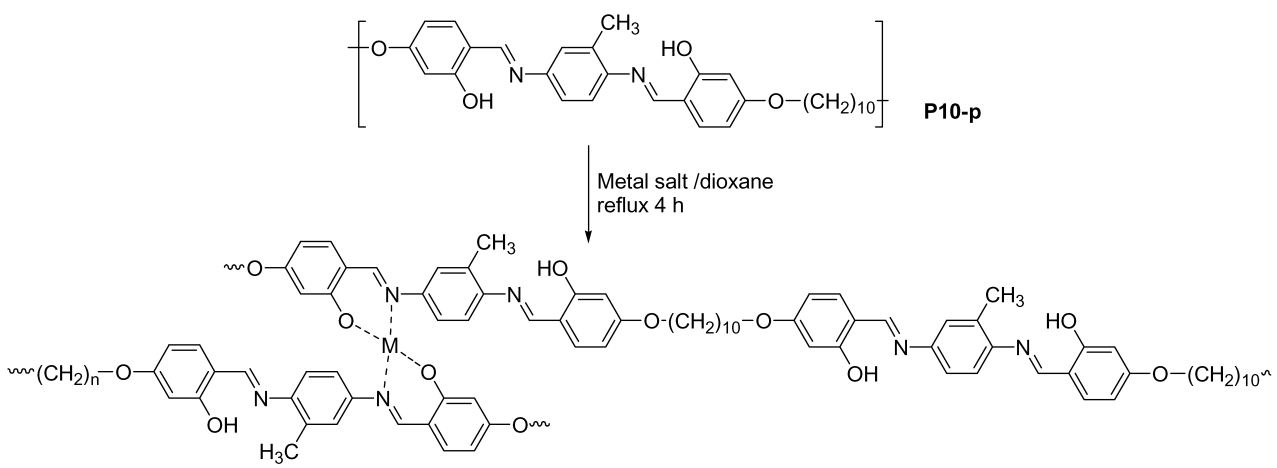
Metal complexation was accomplished in a suspension of the polymer in 1,4-dioxane with the appropriate metal salt [zinc acetate, nickel(II) acetate, vanadyl sulphate, iron(III) chloride or copper(II) acetate] as reported previously [10]. A description of the procedure is given for P10-Zn: Polyazomethine P10-p (1.502 g) was suspended with mechanical stirring in freshly distilled 1,4-dioxane (100 ml) under reflux. Zinc acetate [13 mg, ca. 2 mol of Zn(II) ions per 100 mol of repeating unit] in hot 1,4-dioxane (10 ml) was added dropwise to the above suspension. The suspension was stirred for 2 h under an inert atmosphere. The reaction mixture was cooled and the solid was filtered off and successively washed with 1,4-dioxane, hot water, and methanol. The product was extracted (Soxhlet apparatus) with acetone for 24 h and finally dried under vacuum over P_2O_5 for 24 h at 80 °C to yield the metal-modified polyazomethine. The experimental percentage of metal was determined by atomic emission spectroscopy (see Fig. 2).



Dialdehyde	Diamine	Homopolyazomethine
2	p	P2-p
6	p	P6-p
10	p	P10-p
2	m	P2-m
6	m	P6-m
10	m	P10-m

Dialdehyde (molar ratio)	Diamine (molar ratio)	Copolyazomethine
6 + 10 (1:1)	p	P6/10-p
6	p + m (3:1)	P6-p/m(3:1)
6	p + m (1:1)	P6-p/m(1:1)
6	p + m (1:3)	P6-p/m(1:3)
6 + 2 (1:1)	p + m (1:1)	P6/2-p/m(1:1)

Fig. 1. Schematic representation of the synthetic strategy and repeating unit of target polyazomethines. The figure includes the composition and notation of the synthesised homo- and copolyazomethines.



M	Metal-modified polyazomethine	Experimentally determined metal content [a]
Zn^{2+}	P10-Zn	1.63
Ni^{2+}	P10-Ni	1.08
VO^{2+}	P10-V	1.75
$FeCl^{2+}$	P10-Fe	1.45

(a) Values given in metallic ions per hundred repeating units

Fig. 2. Schematic representation of the synthetic strategy and repeating unit of metal-modified polyazomethines. The figure includes the notation and experimental metal content (given in metal ions per hundred repeating units) calculated by atomic absorption spectroscopy.

Table 1
Polymerisation yields and physical characterisation of homo- and copolyazomethines

	Yield	η_{inh} [a]	Elemental analysis[b]			C=N(st) (cm^{-1})	CH=N δ/ppm
			C	H	N		
P2-p	75	0.40	70.33 (71.12)	5.34 (5.20)	7.46 (7.21)	1635	8.86, 8.71
P6-p	98	0.43	72.15 (72.96)	6.05 (6.35)	6.18 (6.30)	1606	8.84
P10-p	96	0.62	73.80 (74.37)	7.22 (7.25)	5.48 (5.60)	1607	8.78
P2-m	60	0.36	70.30 (71.12)	5.73 (5.20)	7.39 (7.21)	1635	8.89, 8.79
P6-m	50	0.31	72.09 (72.95)	6.17 (6.35)	6.73 (6.30)	1616	8.77, 8.74
P10-m	40	0.29	73.27 (74.37)	7.90 (7.25)	5.90 (5.60)	1612	8.76, 8.74
P6/10-p	96	0.55	73.02 (73.71)	6.59 (6.83)	5.83 (5.93)	1607	8.82
P6-p/m(3:1)	70	0.37	71.57 (72.95)	6.15 (6.35)	6.79 (6.30)	1622	8.74
P6-p/m(1:1)	71	0.28	71.63 (72.95)	6.39 (6.35)	6.12 (6.30)	1618	8.75
P6-p/m(1:3)	73	0.24	71.76 (72.95)	6.52 (6.35)	6.23 (6.30)	1607	8.76, 8.74
P6/2-p/m	71	0.36	71.43 (72.09)	5.89 (5.81)	6.21 (6.73)	1617	8.84, 8.74

[a] Values given in g dl^{-1}. Values were determined in 0.5 g dl^{-1} methanesulfonic acid solutions at 40 °C. Time required for the total dissolution of the polymer was 2 h except those copolyazomethines containing p/m which was 4 h.
[b] Calculated values are given in parenthesis.

2.3. Processing and annealing of the fibres

Fibres were processed in a small-scale melt-extrusion unit that was specially designed in our laboratory [10]. The unit was fitted with a commercial single-hole exit die for engineering polymers of 0.45 mm diameter. Approximately 500 mg of the polyazomethine was loaded and the molten polymer was extruded in the nematic state. The processing temperature of each polymer was selected according to differential scanning calorimetry (DSC) scans and optical microscopy observations. Several experiments were required in each case to obtain fibres of good quality. Pressure was applied by a driven piston using a weight that was varied depending on the viscosity of the extruded polymer. In some cases, a gradual increase of the pressure was required in order ensure a continuous fibre drawing. Monofilaments were spun into air at room temperature either by falling from the end of the exit die under its own weight or by suspending the minimum weight necessary to avoid windup of the fibres. Extrusion rates were dependent on the polymer and ranged from 0.4 to 0.03 mm s^{-1}. The linear density of the fibres was about 1.5–2.8 mg cm^{-1} and diameters were about 0.43–0.50 mm.

Extrusion was accomplished in two ways and these are referred to as methods A and B. Method A involved the introduction of the polymer into the melt-spinning unit previously heated to the processing temperature. Method B involved the introduction of the polymer into the melt-spinning unit at room temperature followed by heating the unit to the processing temperature.

Selected fibre specimens were thermally annealed at 100 °C for 12 h under a longitudinal tension applied by suspending a weight of 110 g from the end of the fibre.

2.4. Techniques

Elemental analyses were performed using a Perkin-Elmer 240C microanalyzer. IR spectra were obtained on a Nicolet 250-FTIR spectrometer using KBr disks dried at 80 °C under vacuum for 1 h. ^{1}H NMR spectra were measured at room temperature with a Varian Unit-300 spectrometer. The samples consisted of polymer solutions in deuterated trifluoroacetic acid and these were studied immediately after preparation. Metal contents were determined by inductively coupled plasma atomic emission spectroscopy using a Perkin-Elmer P-40 spectrometer.

Inherent viscosities (η_{inh}) were determined at a concentration of 0.5 g dl^{-1} of the polymers in methanesulfonic acid at 40 °C using a Cannon–Fenske viscometer. Determinations were carried out immediately after preparation and, wherever possible, values are quoted as an average of five measurements that did not differ from each other by more than 1%.

Thermogravimetric analysis was performed using a TA STD 2960 simultaneous DTA-DTGA instrument at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. Mesogenic behaviour was evaluated by optical microscopy using an Olympus BH-2 polarizing microscope fitted with a Linkam THMS600 hot stage. Thermal transitions were determined by DSC on a Perkin-Elmer DSC-7. Temperatures were read at the maximum of the peaks recorded at a scanning rate of 10 °C min^{-1}. Glass transition temperatures (T_g) were determined at the midpoint of the baseline jump.

XRD measurements were performed with an evacuated Pinhole camera (Anton–Paar) operating with a point-focused Ni-filtered Cu Kα beam. The fibres were held in Lindemann glass capillaries and the patterns were collected on flat photographic film perpendicular to the X-ray beam. The fibre axis was vertical (as indicated in the corresponding photographs) and also perpendicular to the X-ray beam.

Mechanical properties of the fibres, including elastic modulus (EM), tensile strength (TS) and elongation at break (E), were determined at room temperature on a computer-controlled 10002 Lloyd Instrument using uniform fibres of

10 cm length. The fibre was mounted in a PBT clamp whose internal faces were covered with a fine sand paper to avoid slipping during the experiment. Tensile deformation was applied at a crosshead speed of 10 mm min^{-1}. Several specimens of each fibre were tested. Values are averages of at least four individual measurements. Fibre diameters were determined with an electronic micrometer (±0.001 error).

Morphological studies by electron scanning microscopy of fibres were performed using a JSM 6400 instrument. Two types of specimens were studied: fibres fractured on the Instron machine to study the tensile fracture surface, and fibres prepared by the peel-back method to inspect the internal structure. Peel-back fibres were prepared cutting at an oblique angle halfway into their section and subsequently pulling with tweezers to leave an exposed longitudinal internal section of the samples.

3. Results and discussion

3.1. Synthesis and physical characterisation of the polymers

Polymers were prepared by condensing a dialdehyde and a diamine to form the mesogenic core during the polymerisation process (Fig. 1). This strategy has proven to be the most suitable when hydroxy-functionalisation of the resulting polyazomethines is required [14]. Polymerisation was carried out in solution using freshly distilled *N*,*N*-dimethylacetamide as the reaction medium, and LiCl was used to remove the water formed during the polycondensation. We found that in order to achieve reproducible results, it is crucial to exert strict control over the reaction conditions such as the purity of the monomers and solvent, the reaction time, the agitation rate and the temperature. All of these factors play a very important role in determining the molecular weight of the polymer, a parameter that is related to the viscosity of the melt and, therefore, the ease of processing of the polymer.

Polymerisation was monitored by IR spectroscopy by following the disappearance of the carbonyl band due to the monomeric dialdehyde and the appearance of the imine band of the polyazomethine (around 1600 cm^{-1}). ^{1}H NMR spectra taken in deuterated TFA also indicate the formation of an imine group with the presence of a signal at around 8.80 ppm (see Table 1). It can be seen from the data in Table 1 that the introduction of the diamine *m* and/or the shortest alkyl spacer with two carbon atoms causes splitting of the signal corresponding to the imine proton into two overlapping signals.

^{1}H NMR spectra provide useful information about the final composition of the copolymers. Due to their structural similarity, we should not expect differences in the reactivities of the dialdehydes 6 and 10 but in the case of dialdehyde 2 similar reactivity cannot be assumed automatically. Nevertheless, the chemical shift of the $-OCH_2-$ protons is different for dialdehydes 6 and 2, and integration of the corresponding signals indicates that the monomeric dialdehyde ratio incorporated into the copolyazomethine P6/2-p/m is in accordance with the reaction feed mixture. In the case of copolyazomethines p/m, we can infer several conclusions by comparing the signals corresponding to the $-CH_3$ protons. In the spectra of P6-p/m (1:1), we observed two different signals at 2.63 and 2.61 ppm corresponding to the $-CH_3$ protons of the rigid cores of diamines *p* and *m*. The relative peak height ratio implies that the copolyazomethine contains approximately the same molar amount of the two diamine monomers.

Molecular weight and molecular weight distribution of polymers are important aspects with regard to thermal and mechanical properties. However, the lack of solubility of polyazomethines in common solvents restricts the applicability of common techniques such as size exclusion chromatography. In spite of this difficulty, some information in this respect is available from the ^{1}H NMR spectra and viscometry values. In the ^{1}H NMR spectra, signals corresponding to aldehyde terminal groups are detected just above 9.50 ppm. From the ratio between the relative integration of this peak and that corresponding to the imine group, values for the degree of polymerisation for the target polyazomethines are calculated to be approximately 20–30. It must be noted that, because the spectra are recorded in TFA, hydrolysis occurs to some extent and the estimated degrees of polymerisation could well be slightly higher. Inherent viscosity values of the different homo- and copolyazomethines are collected in Table 1. It must be pointed out that both polymerisation yields and inherent viscosities are lower for *m*-diamine-containing polyazomethines. These two experimental parameters taken together might be a result of the *m*-diamine reacting more slowly to give lower molecular weights. However, degrees of polymerisation calculated by ^{1}H NMR do not support this possibility as significant differences are not observed between isomeric *p*- and *m*-homopolyazomethines or in the estimated proportion of p/m monomers in copolyazomethines. These observations can be explained by taking into account two arguments. Firstly, the yields shown in Table 1 were recorded after Soxhlet extraction and the higher solubility of *m*-homopolyazomethines should result in a more efficient removal of the corresponding oligomers. Secondly, the viscosity is related not only to the molecular weight but also to the specific molecular volume and, therefore, comparisons are restricted by the conformational geometry of the polymeric chains.

Metal-complexed mesogenic polyazomethines were obtained according to previously described methods. Due to the low solubility of the parent polyazomethines in common organic solvents, formation of the complexes was carried out in a suspension of the polymer in dioxane with the corresponding metal salt. Polymer P10-p was modified with a theoretical 2% (molar ratio referred to the repeating unit) of metallic centres because it has been previously proved that higher percentages give rise to polymers in

which the anisotropic melt has an extremely high viscosity, a phenomenon that makes the materials very difficult process. In relation to the metal, in a previous publication we incorporated Cu(II) in P10-p [10,13]. On this occasion, we incorporated Ni(II), Zn(II), Fe(III) and V(IV). In all cases, due to the rigidity of the aromatic core, metal ions bind two mesogenic units of different polymeric chains giving rise to partially cross-linked materials [11,12]. However, the geometry around the metal centre is different in all cases [15]. The final metal content was experimentally evaluated by atomic absorption spectroscopy (see Fig. 2) and, as one would expect, it is lower than the theoretically calculated value.

3.2. Thermal characterisation of the polymers

The thermal stability of the polymers was evaluated by simultaneous DTA-TGA under a nitrogen atmosphere and the results are collected in Table 2. All the polyazomethines show good thermal stability with, in general, weight losses above 350 °C associated with thermal decomposition. Nevertheless, it can be concluded that polyazomethines with a higher content of repeating units derived from the *p*-diamine show a slightly higher thermal stability.

Thermal and mesomorphic behaviour were investigated by optical microscopy and DSC. The results are also presented in Table 2. Temperatures were determined from a second heating scan after heating and cooling the sample at 10 °C min^{-1}. In some cases samples were annealed for 1 h just above the melting temperature. As one would expect, homopolyazomethines derived from a *meta*-substituted diamine do not show liquid crystalline behaviour due to the decrease in the linearity of the rigid core structure. Instead, these materials were found to be amorphous polymers whose T_g values depend on the length of the flexible spacer.

From homopolyazomethines containing the *para*-substituted diamine, P2-p shows a very high melting temperature that hinders the formation of a mesophase. However, as the spacer length increases the transition temperatures decrease and the formation of mesophases becomes more favourable. The DSC traces of P6-p and P10-p, recorded after annealing the samples just above the mesophase (200 and 150 °C, respectively), reveal their semicrystalline nature. Two melting endotherms were found for P6-p at 229 and 259 °C; these are associated with recrystallisation processes of the polymeric chains. Both homopolyazomethines P6-p and P10-p developed nematic textures when viewed through crossed polarisers.

The copolymer P6/10-p showed a nematic mesophase texture when viewed through crossed polarisers. This compound formed an amorphous polymer when cooled from the mesophase at 10 °C/min. However, annealing of the sample at 140 °C induces crystallisation and the copolyazomethine melts at 164 °C.

In relation to the copolyazomethine P6-p/m, the DSC

Table 2
Thermal stability and thermal transition data (DSC) of the organic and metal-containing polyazomethines

	TGA (°C)	DTGA (°C)	T_g (°C)	T_m (°C) [ΔH (kJ/mol of repeating unit)]	T_i (°C)	Mesophase
P2-p	360	372	[a]	333 [18]		
P6-p[b]	367	381	65	229 [7], 259 [5]	[c]	Nematic
P10-p[d]	369	383	54[e]	175 [19]	331	Nematic
P2-m	352	370	161			
P6-m	349	362	100			
P10-m	357	369	65			
P6/10-p[f]	372	382	55	164 [3], 187 [0.2]	[c]	Nematic
P6-p/m(3:1)	361	370	71[g]	231 [4], 244 [4]	[c]	Nematic
P6-p/m(1:1)[d]	358	369	82	173 [5], 219 [1], 244 [2]	[c]	Nematic
P6-p/m(1:3)	354	364	83			
P6/2-p/m	353	360	92	250, 260 [2][h]	300[i]	Nematic
P10-Ni	373	385	55	167 [9]	332	Nematic
P10-Fe	358	381	57		336	Nematic
P10-Zn	371	386	58	160 [7]	333	Nematic
P10-V	350	381, 409	57		326	Nematic

TGA: onset of the weight loss in thermogravimetric analysis; DTGA: derivative thermogravimetric analysis; T_g : glass transition temperature; T_m : melting temperature; ΔH : melting enthalpy; T_i : isotropisation temperature.

[a] Transition not detected on the DSC scans.
[b] DSC data recorded after annealing at 200 °C for 1 h.
[c] Decomposition in the mesophase.
[d] DSC data recorded after annealing at 150 °C for 1 h.
[e] Value determined from a sample heated at 250 °C and quenched in liquid nitrogen.
[f] DSC data recorded after annealing at 140 °C for 1 h.
[g] Slow cold crystallisation above T_g.
[h] Overlapped peaks.
[i] Decomposition at the clearing point.

scans reveal the relationship between the degree of crystallinity and the content of the *para*-subtituted diamine p, as evidenced by comparing the homopolymers. The copolymer P6-p/m (1:3) is an amorphous material that, due to the high content of diamine m, does not develop any liquid crystalline phase. However, characteristic threaded nematic textures were identified by optical microscopy for P6-p/m (1:1) and P6-p/m (3:1). The DSC traces of P6-p/m (1:1) indicate that the behaviour is dependent on the thermal treatment. In the first experiment, a sample was heated above the melting temperature and cooled down at 10 °C min^{-1}. On heating the sample again, two melting endotherms were observed at 232 and 250 °C. In a second experiment, a sample was annealed at 150 °C for 1 h and, after cooling, a subsequent heating cycle gave rise to an additional endotherm at 173 °C. P6-p/m (3:1) shows a slow cold crystallisation process between the T_g and the T_m. For the three copolyazomethines P6-p/m, T_g values are intermediate between those of P6-p and P6-m, indicating a random distribution of monomers *p* and *m* along the polymeric chain.

From these results one might conclude that, in terms of the reduction of the melting temperature and stabilisation of the mesophase, copolymerisation with different diamines is less effective than copolymerisation with aldehydes with different methylenic spacers. For this reason, one last copolyazomethine, denoted P6/2-p/m (1:1), incorporating diamines *p* and *m* in a 1:1 ratio was prepared by reacting with a mixture of dialdehydes 2 and 6 in a 1:1 ratio. The resulting material is also a semicrystalline polymer with a nematic mesophase, although in this case the transition temperatures are higher with the polymer melting at 250 °C.

All of the metal-modified polyazomethines show similar T_g values at around 55 °C (Table 2). Melting is associated only with those metal-containing polymers that undergo cold crystallisation. This phenomenon indicates the amorphous nature of the metal-containing polymers. All the polymers show a highly viscous granular texture that was identified as being due to a nematic mesophase. Furthermore, metal complexation does not significantly affect the thermal stability, a fact deduced from the TGA measurements.

3.3. Fibre processing and characterisation

As a consequence of the previous thermal study, only nematic polymers were considered as suitable candidates for the preparation of fibres. Of these samples, P6-p, P10-p, P6/10-p and metal-modified systems were extruded into fibres. Despite showing a nematic mesophase, P6-p/m (3:1), P6-p/m (1:1) and P6/2-p/m were not considered for further studies due to their high melting temperatures, which are comparable to those of P6-p. As described later, the high temperatures required to extrude P6-p yielded fibres with poor mechanical properties. For this reason, the aforementioned polyazomethines were not processed.

The extrusion temperature was empirically selected after several initial tests. For each polymer, fibres were processed at different temperatures above the melting temperature. The final conditions, which are detailed in Table 3, were chosen by taking the quality of the fibre as the selection criterium. On this basis fragile and rough fibres with a yellow coloration, characteristics that indicate incomplete melting of the polymer inside the extrusion equipment, were rejected. Alternatively, smooth fibres with superficial gloss and constant diameter were considered as optimum materials for subsequent studies.

In addition, two different procedures were followed to extrude fibres (see Section 2). In method A, the extrusion equipment was heated to the processing temperature prior to introduction of the polymer into the unit. This procedure was used successfully in previous studies. In method B, the polymer was introduced into the extrusion equipment at room temperature and then heated to the processing temperature. Differences in the procedures affect the time the polymer is in the molten state inside the extrusion equipment, conditions under which it is known to experience an increase in molecular weight [9,10]. The increase in the molecular weight also results in an increase in the viscosity of the molten polymer. For this reason, the processing temperatures were higher when procedure A was followed. Nevertheless, it was shown that the change in procedure did not have an appreciable effect on the quality of the fibres.

In general, during the extrusion procedure and due to the aforementioned increase in the viscosity in the molten state, a gradual increase in temperature was required to maintain a continuous flow through the spinneret hole. The required temperature increase was greater for P6/10-p. However, in spite of the high temperature and the slow drawing rate, the extruded fibres of this copolyazomethine had a good appearance. Extrusion rates were dependent on the polymer and ranged from ca. 0.1 to 0.4 mm s^{-1} for homopolyazomethines P6-p and P10-p, and from 0.03 to 0.05 mm s^{-1} for copolyazomethine P6/10-p and metal-containing polyazomethines. The linear density of the fibres was in the range 1.5–2.8 mg cm^{-1} and diameters ranged from 0.43 to 0.50 mm. The exception was the Ni(II) derivative, P10-Ni, whose linear density and diameter values were somewhat higher at 4.5 mg cm^{-1} and 0.66 mm, respectively.

Selected specimens of these fibres were subjected to thermal annealing at 100 °C under an applied longitudinal tension—apart from the metal-containing systems. Processing of metal-modified polyazomethines was difficult because of the presence of cross-linking, which imparts a higher viscosity to the anisotropic melt. In some cases, rough and knotted fibres were obtained and it was not possible to obtain good filaments of compounds such as P10-Fe. The reason for this is that metal-containing fibres were not annealed. In general, small changes in the length and diameter of the fibres were observed after annealing but their weight and appearance remained the same.

Table 3
Processing conditions, viscometry and tensile properties of as-spun and annealed fibres

					DSC			Tensile Properties		
Polymer	Fibre	Method	Processing T	η_{inh} [a]	T_g (°C)	T_c (°C)	T_m (°C)	EM (GPa)	TS (MPa)	E (%)
P6-p	F6-P1	A	280	[b]	60		235 [1]	7.2	175	2.6
	F6-T1				85[c]		235 [0.1]	7.4	100	1.5
	F6-P2	B	260	[b]	[d]		227 [2]	3.7	110	2.6
	F6-T2				[d]		226 [2]	4.5	105	1.5
P10-p	F10-P1	A	235	>1.94	52	87 (6)	167 [4]	11.7	470	5.1
	F10-T1				[d]		169 [12]	18.6	875	7.1
	F10-P2	B	195	>1.13	52	81 (7)	176 [9]	10.4	380	5.1
	F10-T2				[d]		168 [11]	12.6	590	7.4
P6/10-p	F6/10-P1	A	250	>0.83	54			11.6	520	5.6
	F6/10-T1				53			15.4	785	5.7
	F6/10-P2	B	195	>0.78	57			2.9	125	6.3
	F6/10-T2				55			2.9	100	4.2
P10-Zn	F10-Zn	B	200		58			7.0	260	4.9
P10-Ni	F10-Ni	B	195		54			1.5	55	5.6
P10-V	F10-V	B	200		54			4.2	220	8.7

T_g : glass transition temperature, T_c : cold crystallisation temperature, T_m : melting temperature. In brackets values of the associated transition enthalpies given in kilojoules per mole of repeating unit. EM: elastic modulus; TS: tensile strength; E : elongation at break.

[a] Values given in g dl^{-1}. Values were determined in 0.5 g dl^{-1} methanesulfonic acid solutions at 40 °C. Time required for the total dissolution of the fibre was between 7 and 20 h. Degradation of the polymer was observed during the determination of inherent viscosity.

[b] Decomposition of the sample takes place before complete solubilisation.

[c] Extended over a wide temperature interval.

[d] Not detected.

As-spun and annealed fibres were characterised by IR and ^{1}H NMR with the aim of detecting any changes in the structure or composition of the polyazomethines. The only differences encountered were associated with the increase in the molecular weight after processing, a change deduced from the disappearance of terminal aldehyde group signals in the ^{1}H NMR spectra. Degradation, decomposition or cross-linking of the materials was not evident in these experiments, although it is impossible to rule out the occurrence of the latter process.

The thermal stability of the fibres was evaluated by TGA and was found to be similar to the parent polymers. Fibres were also investigated by DSC and data were collected during the first heating scan in order to gain information about the effect of the processing conditions on the thermal properties.

DSC data obtained from fibres of polyazomethine P10-p are consistent with previously reported results. The as-spun fibres are amorphous materials in which the nematic order has been frozen. T_g values were comparable with those of the parent polymer. On heating the sample, a cold crystallisation was detected around 85 °C and the crystalline fraction formed during this process melted at 170–175 °C. Annealed fibres did not show a T_g and only melting of the fibre was observed because annealing under tension induced crystallisation.

Fibres extruded from copolymer P6/10-p were amorphous but, unlike the fibres of P10-p, they did not undergo a cold crystallisation process on heating. Furthermore, tension annealing at 100 °C did not appear to induce crystallisation nor did it modify the amorphous character of the fibres.

As-spun fibres of polyazomethine P6-p were obtained as semicrystalline materials whose DSC scans revealed the existence of a T_g but not a cold crystallisation prior to the melting transition. In DSC scans of fibre F6-P2, the T_g cannot be observed and only the melting endotherm is evident. The higher enthalpic value associated with the melting transition indicates the higher crystallinity of this fibre. Extrusion from a nematic melt is expected to give amorphous fibres in which the uniaxial molecular orientation of the mesophase is frozen. As-spun fibres of P6-p were not completely amorphous and so it seems reasonable to assume a poor initial molecular orientation—a situation confirmed by X-ray diffraction.

As-spun metal-containing fibres show very similar behaviour. All are amorphous materials with T_g values around 55 °C and there is no evidence of cold crystallisation or melting processes.

3.4. Mechanical properties and structural study of the fibres

The objective of this study was to relate the mechanical properties to the microstructure of the fibres. In order to accomplish this goal, selected fibres were investigated by X-ray diffraction and scanning electron microscopy. Tensile properties of the materials are listed in Table 3.

In accordance with previous reports [10], SEM images of fibres of polyazomethine P10-p reveal a fibrous morphology

with a uniaxial orientation of the molecules in the direction of the fibre axis and a good lateral cohesion. Molecular orientation is induced both in the outer surface and in the centre of the fibre. X-ray diffraction data obtained for as-spun and tension-annealed fibres of P10-p are also in full agreement with previous reports [9]. The X-ray patterns of as-spun fibres are consistent with an amorphous material in which the nematic ordering has been frozen and the molecules are oriented along the extrusion direction. X-ray patterns of thermally annealed fibres contain multiple reflections, a situation indicative of a crystalline material. These diagrams have been indexed on the basis of a primitive triclinic lattice with parameters $a_o = 0.630$ nm, $b_o = 0.476$ nm, $c_o = 3.067$ nm, $\alpha = 73°$, $\beta = 59°$, $\gamma = 75.5°$. The cell contains one repeating unit in a fully extended conformation aligned along the c_o axis of the crystal. Indeed, the experimentally measured c parameter is in good agreement with the length of the fully extended repeating unit estimated from Dreiding stereomodels (about 3.2 nm). This value is also in good agreement with the effective molecular length in the frozen nematic phase of the as-spun fibres (3.1 nm). The value is deduced from the small-angle four-point pattern and is measured as the local periodicity along the meridian (direction of the molecular axis). We can conclude that annealing induces a dramatic increase in crystallinity and molecular orientation.

As-spun fibres of P10-p have good mechanical properties, especially when their semiflexible character is taken into account. On annealing, a significant improvement in the mechanical properties is achieved due to the reinforcement of the molecular orientation under tension and the increase in crystallinity. We must emphasise that the values for the mechanical properties obtained for these fibres are an improvement on the best values obtained so far for the same polymer, in particular the TS and elongation at break [16]. On comparing the new results, we also observed that the relative improvement in the mechanical properties on annealing is not significant when compared to the relative improvement seen in previous publications, mainly for the EM [9]. Those previous values were obtained with fibres extruded at 190 °C in a commercial extruder fitted with an exit die specially designed for liquid crystal polymers. Apart from differences in processing, the polyazomethines used in both cases had a different average molecular weight, as inferred from their inherent viscosity values (0.45 g dl^{-1} *versus* 0.62 g dl^{-1}). It is known that one of the factors affecting the improvement in the tensile properties is the gain in molecular weight during processing. However, it is also known that the mechanical properties increase with molecular weight up to a value above which the influence is negligible. Therefore, we relate the enhanced mechanical properties and the less marked influence of the annealing process with the higher molecular weight of the P10-p polyazomethine reported here.

The morphology of fibres of copolyazomethine P6/10-p is similar to that of P10-p, i.e. a fibrillar microstructure and a good orientation along the longitudinal direction of the fibre, as observed from the peel-back SEM images (Fig. 3(a)). The image of the tensile fractured surface shows a slow energy-absorbing fibrillar fracture (Fig. 3(b)). Changes in the morphology of the fibres were not observed upon thermal annealing. Comparison of X-ray diffraction patterns of fibres F6/10-P1 and F6/10-P2 reveal significant differences between them. The diagram for F6/10-P1 consists of diffuse maxima at the equatorial region and this corresponds to a well-oriented structure attained by freezing the nematic order during processing (Fig. 3(c)). Thermally annealed F6/10-T1 shows a very similar diffraction pattern and is consistent with a highly oriented nematic ordering, which in this case coexists with a minor crystalline phase revealed by the presence of some sharp equatorial reflections (Fig. 3(d)). In both as-spun and annealed fibres the effective molecular length measured by X-ray diffraction is 2.9 nm. The decrease in this value compared to fibres of P10-p is reasonable bearing in mind the contribution of the shorter hexamethylene spacer in this copolymer. In accordance with the DSC data for these fibres, the results indicate that tension annealing does not induce an efficient crystallisation of the fibre. The X-ray diagram of as-spun fibres F6/10-P2 show diffuse maxima consistent with a nematic ordering, but analysis of the diagram indicates a poor molecular orientation with a deviation of the molecules from the extrusion direction (Fig. 3(e)). X-ray analysis of the thermally annealed fibre F6/10-T2 indicates the presence of a small amount of a crystalline phase (Fig. 3(f)). We presume that the processing conditions of these fibres are not adequate and do not induce a satisfactory uniaxial molecular orientation. This presumption was confirmed by tensile experiments. F6/10-P1 and F6/10-T1 show good mechanical properties that are comparable to the fibres of polyazomethine P10-p. However, the tensile properties of F6/10-P2 are very poor and can not be improved by thermal annealing.

As-spun fibres of P6-p homopolyazomethines have an internal structure with numerous imperfections. Imaging of fibres prepared by the peel-back method reveal that the fibre centre has a high content of voids where molecular orientation is distorted (Fig. 4(a) and (c)). These voids should act as weak points where the fracture can be induced and propagated. We correlate this internal structure with a certain amount of thermal degradation under an oxidising atmosphere induced by the high processing temperatures, with degradation producing off-gassing that results in the formation of bubbles in the melt. In order to corroborate this possibility, the thermal stability of the material at 280 °C was determined by TGA. After 60 min under oxidising conditions (air atmosphere) a weight loss of 1% was observed. However, under inert conditions (nitrogen atmosphere) the sample weight remained constant. Thermal annealing under tension was found to significantly reduce the void content because the bubbles are deformed and coalesce. However, even under these conditions peel-back

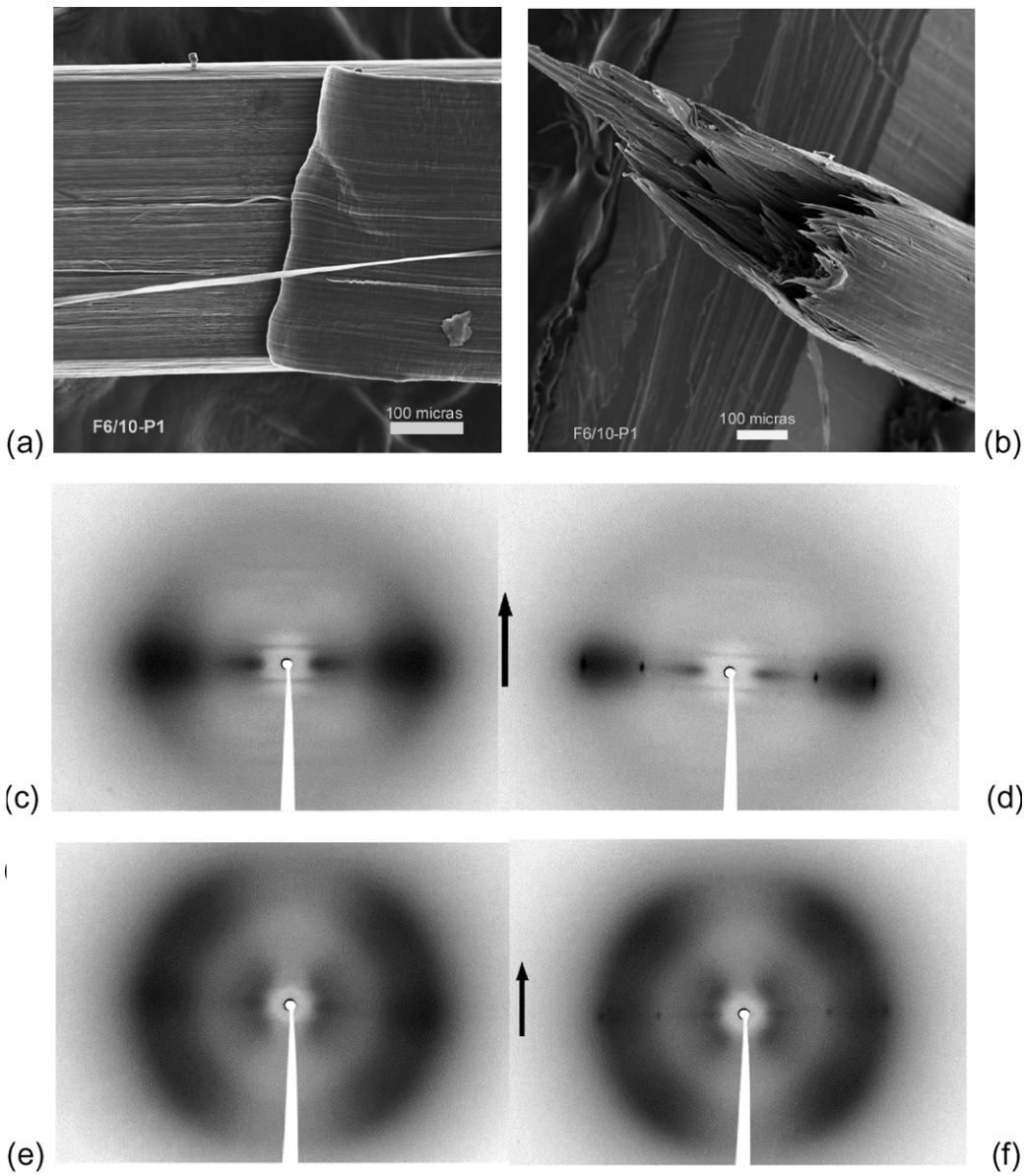


Fig. 3. Fibres extruded from P6/10 polyazomethine. SEM photographs of F6/10-P1 fibres: (a) sample prepared by the peel-back method and (b) tensile fracture surface. X-ray diffraction patterns of fibres as-spun and annealed at 100 °C for 12 h: F6/10-P1 (c), F6/10-T1 (d), F6/10-P2 (e) and F6/10-T2 (f). The arrow indicates the longitudinal axis of the fibre.

SEM images still reveal a lack of uniformity at the centre of the fibre (Fig. 4(b) and (d)). X-ray patterns of F6-P2 and F6-T2 fibres show multiple reflections with an almost symmetrical ring shape. Such a pattern is consistent with a high degree of crystallinity and low degree of molecular orientation (Fig. 4(e) and (f)). Annealing under tension does not improve either the crystallinity or the molecular orientation of the fibre. The imperfect quality of the fibres explains the poor values found for the tensile properties. These fibres can be classified as fragile and variation of the processing conditions does improve the EM but not the tenacity, which depends mainly on the material structure. Modification of the processing conditions (i.e. changing from method A to method B) can not prevent the presence of the voids where the fracture originates. We believe that shortening the length of the flexible spacer results in an increase in the melting temperature and, therefore, of the processing temperature. This property gives rise to fibres of poor quality—probably due in part to degradation during processing.

Previous work on Cu(II)-modified P10-p showed that the processing of this polyazomethine gives rise to highly oriented fibres in which crystallinity is promoted by tension annealing. This type of copper(II) crosslinking resulted in an improvement of the mechanical properties [10,13]. The introduction of other metal atoms into P10-p gave rise to fibres with structural imperfections in that the molecular orientation had been disrupted and tensile fracture occurred.

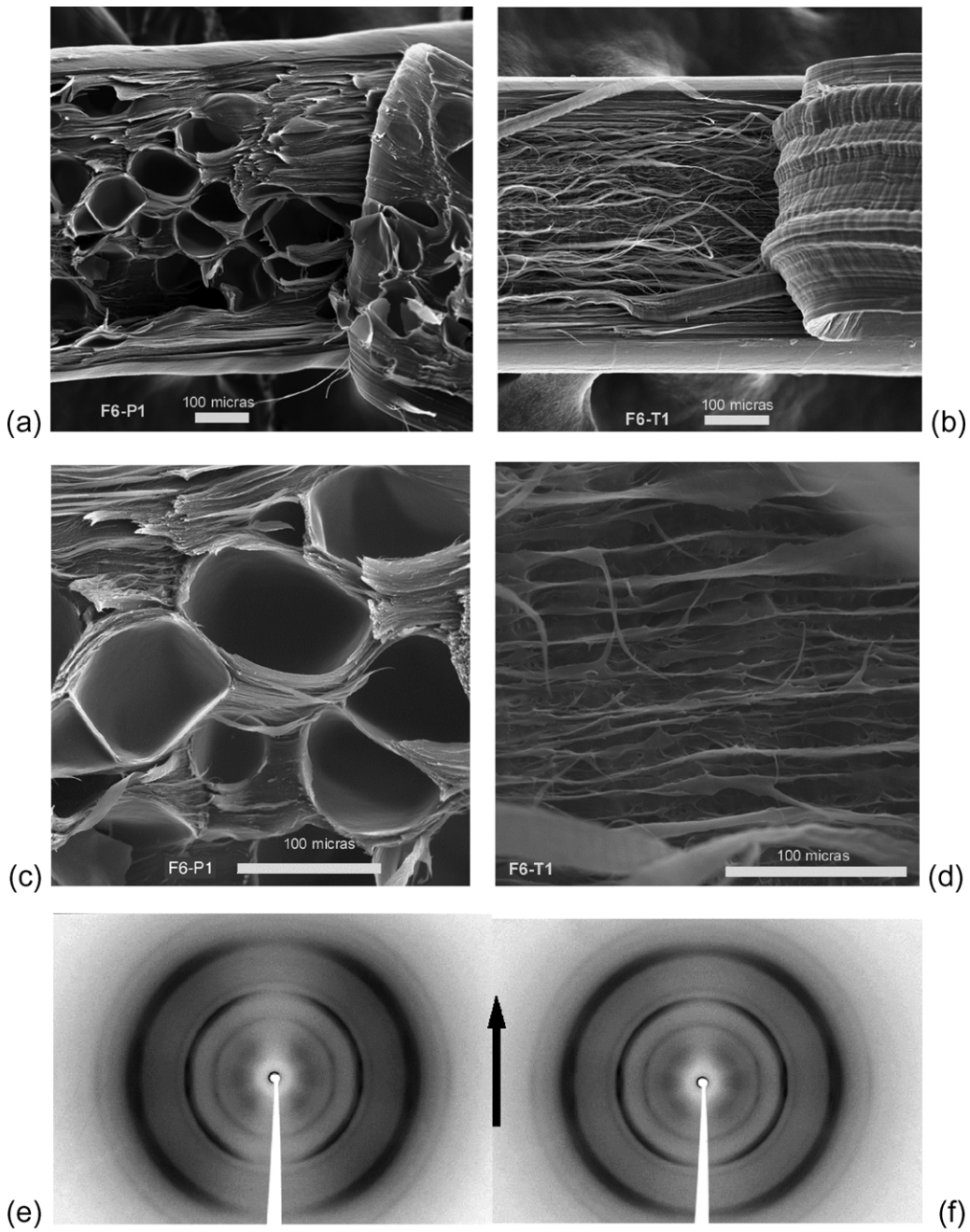


Fig. 4. Fibres extruded from P6 polyazomethine. (a) and (c) SEM photographs of as-spun fibres F6-P1 prepared by the peel-back method. (b) and (d) SEM photographs of annealed fibres F6-T1 prepared by the peel-back method. X-ray diffraction patterns of as-spun and annealed fibres: F6-P2 (e), F6-T2 (f), the arrow indicates the longitudinal axis of the fibre.

X-ray patterns, which are closely related to that of the parent P10-p, show, at wide angles, diffuse maxima located in the equatorial region together with a four-point pattern at low angles (Fig. 5). Diagrams are consistent with a nematic arrangement with smectic C-like cybotactic domains. The effective molecular length deduced from the four-point pattern (periodicity measured along the meridian) is 3.1 nm for the Zn(II) and V(IV) complexes, the same value as for the metal-free fibre. In the case of the Ni(II) material it proved impossible to obtain properly oriented patterns (see below), which precluded the determination of this parameter. It can also be deduced that fibres drawn from the nematic melt show a degree of orientation that depends on the metal. The orientation is high for F10-Zn, lower for F10-V and poor for F10-Ni. In spite of the oriented structure, and contrary to the effect observed for Cu(II)-modified P10-p fibres, incorporation of Zn(II), Ni(II) or V(IV) ions into the microstructure of the fibres has an adverse effect on the mechanical properties when compared to the properties of the parent P10-p polyazomethine. These experimental

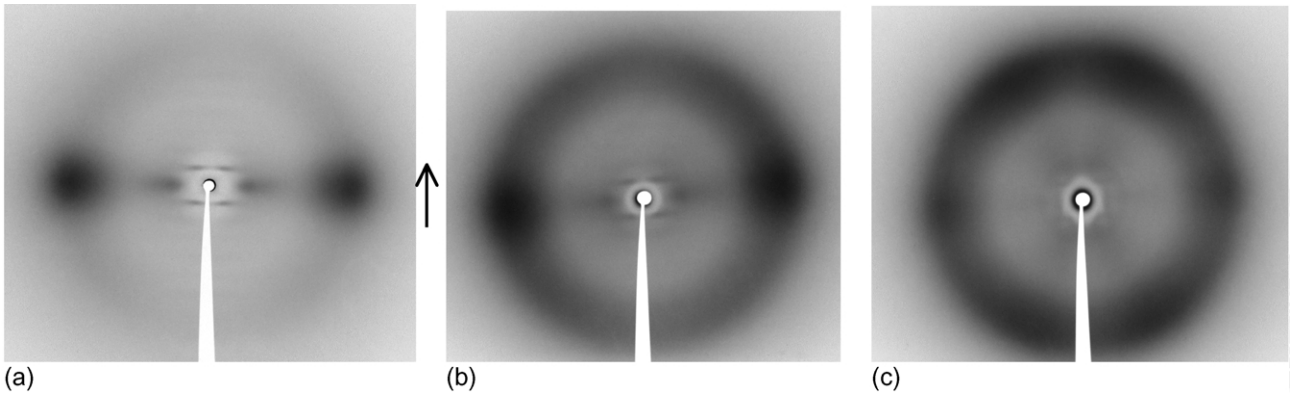


Fig. 5. X-ray diffraction patterns of as-spun metal-containing fibres: F10-Zn (a), F10-V (b) and F10-Ni (c). The arrow indicates the longitudinal axis of the fibre.

findings are in agreement with the structural imperfections observed in the fibres. The differences between these fibres and Cu(II)-modified ones can be mainly explained in terms of differences in the average molecular weight of the parent polymers and the increase in the nematic melt viscosity upon metal crosslinking. The aforementioned parent polymer used for the preparation of Cu(II)-fibres had a lower molecular weight than the parent polymer used for the preparation of Zn(II), Ni(II) or V(IV)-fibres. Our conclusion is that only with moderate molecular weight systems is the incorporation of metal cross-links a suitable option to process fibres with desirable mechanical properties. Otherwise, the viscosity of the metallomesogenic polyazomethine is too high for the polymer to be processed in an appropriate manner.

4. Conclusions

The processing of oriented nematic fibres with high mechanical properties by melt extrusion requires polymers with moderate melting temperatures in order that the fluid mesophase develops before decomposition takes place. We have investigated different structural modifications in semiflexible hydroxy-functionalised polyazomethines in order to gain knowledge concerning the effect of these parameters on the extrusion process and the mechanical properties of the fibres. One of the approaches undertaken involved shortening the length of the flexible spacer in an attempt to render stiffer polymers with improved mechanical properties. This structural modification had an adverse effect on the melting temperature. The hexamethylenic spacer still yields a nematic polyazomethine, although it was found that the polymer requires a high extrusion temperature, which causes off-gassing and formation of voids within the fibres during the processing of the nematic melt. These defects within the microstructure of the fibre had an adverse effect on the tensile properties of the resulting fibre. The second approach involved alteration of the coaxiality by incorporation of a *m*-phenylenediamine monomer. This change gave amorphous homopolymers that did not show mesomorphic properties. Furthermore, copolymerisation with *m*- and *p*-phenylenediamine comonomers does not markedly reduce the melting temperature to yield easily processable materials and, as such, does not represent a viable strategy.

Therefore, we conclude that to melt-extrude fibres with the desired mechanical properties from hydroxy-functionalised polyazomethines, the flexible spacer should be sufficiently long to access milder thermal processing conditions. The last approach, involving copolymerisation with aldehydes having different spacer lengths, appeared to be the best strategy to combine moderate melting temperatures and structural stiffness without dramatically affecting the mechanical properties.

The results also show that the molecular weight of the resulting polymers is a determining factor under any thermal treatment due to the chemical activity of the hydroxy-functionalised polyazomethines. It is assumed that the initial molecular weight of the polymer has to be moderate in order to have an easily processable material. Due to the dynamic nature of the polymers, the properties of the polyazomethines and those of the fibres change during the extrusion process and any subsequent thermal treatment gives rise to a substantial improvement.

Finally, preliminary results on metal-containing polyazomethines indicate that, to obtain fibres with improved the mechanical properties, metal-cross-linking is only an appropriate strategy when considering parent polymers of moderate molecular weights. Nevertheless, further efforts will be made to gain a better understanding of the influence of the metal on the mechanical properties.

Acknowledgements

This work was supported by the CICYT Spanish projects MAT99-1009-C02 and MAT2000-1293-C02. We are grateful to Prof. J.A. Puértolas from the Department of Materials Science and Technology of the University of Zaragoza for

kindly allowing us to use the Tensile Instrument as well as for technical assistance in operating it.

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[16] Values obtained for as-spun fibres were 8.9 GPa, 252 MPa and 3.3% for the elastic modulus, tensile strength and elongation at break, respectively. For thermally annealed fibres under tension the corresponding values were 18.4 GPa, 388 MPa and 2.2% Data taken from Ref. [9].