Polymer 50 (2009) 2048–2057

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Crystalline structure and crystallization of stereoisomeric polyamides derived from arabinaric acid

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ARTICLE INFO

Article history:
Received 26 November 2008
Received in revised form
4 February 2009
Accepted 11 February 2009
Available online 20 February 2009

Keywords:
Arabinaric-derived polyamides
Sugar-derived polyamides
Optically active polyamides

ABSTRACT

The pair of stereoisomeric polyamides PA-6DAr and PA-6LAr, as well as the racemic stereocopolyamide PA-6DLAr was synthesized from hexamethylenediamine and 2,3,4-tri-*O*-methyl-arabinaric acid (D, L and their equimolar mixture, respectively). All these polyamides were aregic, thermally stable and display high crystallinity. The combined analysis by X-ray and electron diffraction revealed that the all three polyamides adopted the same crystal structure, which consists of a rhombic lattice with the chains in a highly contracted conformation capable of accommodating efficiently the sugar moiety in the space. The Avrami kinetic analysis revealed that copolyamide PA-6DLAr crystallized isothermally much slower than the optically homogeneous polyamides. A parallel study carried out on the racemic mixture of PA-6DAr and PA-6LAr evidenced that this mixture has a crystal structure and displays a thermal behavior similar to their separated components, and that its crystallization rate is intermediate between them and the racemic copolyamide PADLAr.

1. Introduction

Polymers based on naturally occurring products are of interest not only for their renewable character but because they may offer novel technical possibilities and improved properties [1]. Among the different natural sources, carbohydrates stand out as highly convenient raw materials because they are inexpensive and readily available, and because they are unique in providing great chemical and stereochemical diversity [2,3]. In this regard, polyamides containing sugar-derived units are being extensively investigated with the aim of adding hydrophilicity and biodegradability to the excellent pattern of properties characteristic of conventional polyamides. The advances attained in the research of polyamides made from compounds derived from carbohydrates have been reviewed [4–6].

A feature of particular interest in connection with the behavior of carbohydrate-derived polyamides is crystallinity, a property that is usually thought to be closely associated to chain stereoregularity. AABB-type polyamides produced by conventional polycondensation methods will be stereoregular provided that their monomers have a 2-fold axis of symmetry; otherwise they may enter the polymer chain in two opposite orientations giving rise to aregic chains. Such imposed symmetry restriction is fulfilled only by a reduced number of monosaccharide configurations, specifically *threo*, *manno* and *ido*. Nevertheless, stereoregular AABB-type polyamides derived from non-centrosymmetric D-glucaric acid have been recently prepared by Kiely et al. using synthetic methods able to discriminate the two carboxyl groups of the diacid in their reactivity toward the aliphatic diamine [7,8].

Within the framework of the systematic investigation that we currently have under course to explore the potential of the sugar-based polyamide family, a number of both stereoregular and non-stereoregular AABB-type polyamides have been synthesized from carbohydrate-derived monomers with the hydroxyl side groups protected as methyl ethers, and they have been fully characterized. These include polyamides made from either α,ω-diaminoalditols or aldaric acids of 4, 5 and 6 carbon atoms [9–12]. Along these studies the idea that stereoregularity and crystallinity of these systems do not correlate with each other has emerged. Whereas stereoregular polytartaramides (polyamides derived from either D or L-threaric acid, *i.e.* tartaric acid) were found to be semicrystalline polymers displaying well-defined melting transitions [13,14], polyamides built from 1,6-diaminomannitol did not show any sign of crystallinity despite they are also stereoregular [12]. On the contrary, *aregic* polyamides made from arabinaric or xylaric acids, were

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doi:10.1016/j.polymer.2009.02.014

found to display a well-developed crystallinity, which is a highly unexpected result [15]. These results led to conclude that monomer configuration cannot be the only factor determining the ability of the sugar-containing polyamides to crystallize and that further investigation is needed to elucidate this issue.

In this work we report on the crystallization and crystal structure of polyamides made from 1,6-hexamethylenediamine and either D- or L-arabinaric acid with the OH side groups protected as methyl ether (PA-6DAr, PA-6LAr and the racemic stereocopolymer PA-6DLAr). These poly(hexamethylene 2,3,4-tri-*O*-methyl arabinaramide)s, can be envisaged as polyamides 6,5 with every backbone carbon of the diacid unit bearing a methoxy side group. The study is mainly focused on the comparative evaluation of the crystal structure and crystallization kinetics of the two enantiomorphs and the stereocopolymer with the aim of affording experimental evidence on the influence exerted by configuration on crystallinity and crystallizability of this class of sugar-derived polyamides.

2. Experimental

2.1. Materials and methods

Chemicals were all used as purchased from Aldrich Chemical Co. Solvents were dried and purified, when necessary, by appropriate standard procedures. ^{13}C NMR spectra were registered at room temperature in a Bruker AMX300 spectrometer. Measurements were made under proton decoupling conditions at 75 MHz. Spectra were taken in $CDCl_3$ solutions with sample concentrations about 3% (w/v), and the number of accumulated scans was 10,240. Differential scanning calorimetry (DSC) measurements were carried out on a Perkin–Elmer calorimeter (Pyris 1) calibrated with indium under a nitrogen flow of 20 mL min^{-1} and using 4–6 mg of powder samples. Melting experiments were carried out at a heating rate of 10 °C min^{-1} and glass transition temperatures were determined at a heating rate of 20 °C min^{-1} from samples quenched from the melt. Isothermal crystallization was accomplished by heating the samples for 5 min above T_m to erase all previous thermal history and then quenched at the nominal rate of 80 °C min^{-1} to the selected crystallization temperature T_c. The samples were held at T_c for the required time to develop the maximum detectable crystallinity. Data taken during this isothermal run were used to perform the Avrami analysis. After the isothermal run was completed, the samples were heated from T_c in order to register their fusion behavior. The melting peak temperatures observed after isothermal crystallization were used to calculate the equilibrium melting temperatures. Polarized optical microscopy (POM) was performed using an Olympus BX51 microscope provided with a digital camera and an image analysis system. A hot-stage Linkam THMS 600 provided with a nitrogen cooling system was used for melting-crystallization experiments. Crystallized films were produced by melting the polymer between two microscope cover slides, maintained at the melting temperature for 3 min and then **quickly** cooled down to the selected crystallization temperature. Cast films were produced at room temperature by slow evaporation of formic acid or chloroform solutions (10%, w/v). X-ray diffraction patterns were obtained with a modified Statton camera using Nickel-filtered Cu-K$_\alpha$ radiation of wavelength 1.542 Å, and they were calibrated with molybdenum sulfide ($d_{002} = 6.147$ Å). Oriented fibers were obtained by stretching the cast films with a tensiometer (Minimat, Polymer Laboratories) at constant strain rate and temperatures well above T_g. Density of crystallized samples was determined by the flotation method using mixtures of aqueous KBr solution and water. Electron microscopy observations were carried out on a Phillips-Tecnai instrument operating at 80 and 100 kV for bright field (digital camera attached) and electron diffraction modes, respectively. Lamellar crystals were prepared by crystallization of the polyamides from diluted solutions (0.1% w/v) in glycerin at 130 °C. Crystals were recovered by centrifugation and after repeating washing with 1-butanol, they were placed on electron microscope carbon-coated grids for observation. Preparations to be examined in the bright field mode were shadowed with platinum-carbon at an angle of approximately 15°. Electron diffraction patterns were recorded in the selected area mode from non-shadowed samples, and they were internally calibrated with gold ($d_{111} = 0.235$ nm).

2.2. Polymer synthesis

The synthesis of polyamide PA-6LAr by polycondensation of pentachlorophenyl ester of 2,3,4-tri-*O*-methyl-L-arabinaric acid with hexamethylenediamine (HMDA) in *N*-methylpyrrolidone (NMP) has been recently described [15]. In the present work, the synthesis of the pair of L- and D-homopolyamides and the racemic stereocopolyamide PA-6DLAr was carried out from the corresponding optically pure enantiomeric arabinaric acids or their equimolar mixture by the same procedure but using *N*,*N*-dimethylformamide (DMF) as solvent according to the following procedure:

To a stirred solution of HMDA (2 mmol) in dry DMF (4 mL) containing triethylamine (0.5 mL) was added the corresponding pentachlorophenyl ester of the 2,3,4-tri-*O*-methyl-D- or L-arabinaric

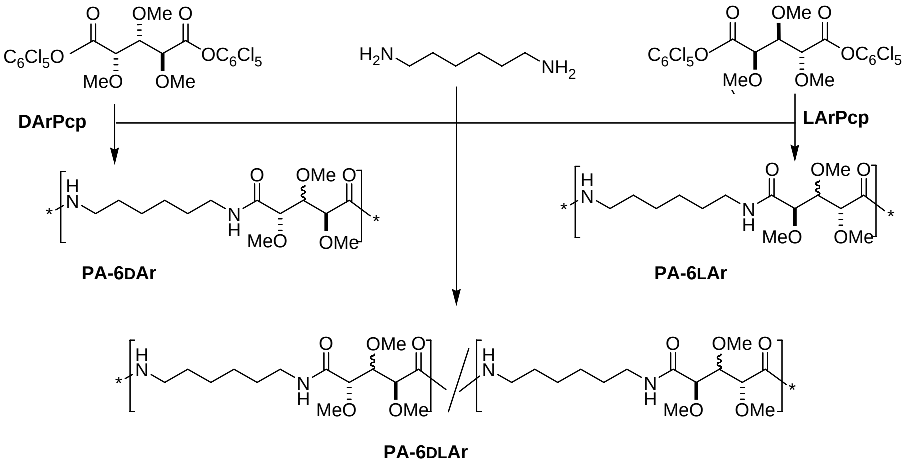

Fig. 1. Synthesis scheme of polyamides PA-6Ar.

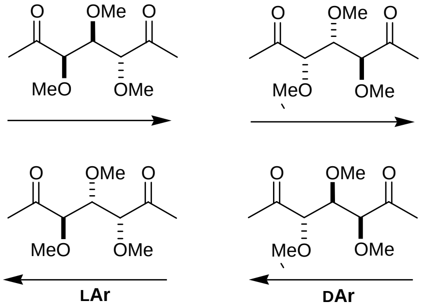

Fig. 2. Possible spatial structures of the arabinaric units along a PA-6Ar polyamide chains depending on their orientation and configuration.

acid, or their equimolar mixture (2 mmol), and the solution was stirred at 60 °C for 5 days. The mixture was then poured into *terc*-butyl-methyl ether (~200 mL) and the suspension was stirred, filtered and washed successively with *terc*-butyl-methyl ether, methanol, and diethyl ether. Finally, the solid was dried under vacuum at 40 °C.

Poly(hexamethylene-2,3,4-tri-O-methyl-L-arabinaramide) PA-6LAr. Yield 62%, Spectroscopic data and elemental analysis identical to those described in reference [15].

Poly(hexamethylene-2,3,4-tri-O-methyl-D-arabinaramide) PA-6DAr. Yield 58%, IR: ν_{max} 1659 (amide I), 1538 cm^{-1} (amide II); ^1H RMN ($CDCl_3$, 300 MHz): δ 6.91 (bs, 1H, NH), 6.50 (bs, 1H, NH), 3.94–3.70 (m, 2H, H-2, H-4), 3.47–3.22 (m, 10H, H-3, 3 OMe), 1.64–1.30 (m, 12H, 6 CH_2). ^{13}C (75 MHz), δ 170.3, 170.2 (CO), 82.2, 81.8, 81.2 (C-2,/C-3/C-4), 61.1, 59.5, 58.2 (3 OMe), 39.0, 29.5, 26.4 (CH_2). Anal. Calcd for $C_{14}H_{26}O_5N_2\cdot 0.25\ H_2O$: C, 54.98; H, 8.40; N, 9.16. Found: C, 54.65; H, 8.60; N, 9.10.

Poly(hexamethylene-2,3,4-tri-O-methyl-DL-arabinaramide) PA-6DLAr. Yield 53%, IR: ν_{max} 1654 (amide I), 1540 cm^{-1} (amide II); ^1H RMN ($CDCl_3$, 300 MHz): δ 6.93 (bs, 1H, NH), 6.51 (bs, 1H, NH), 4.00–3.60 (m, 2H, H-2, H-4), 3.47–3.20 (m, 10H, H-3, 3 OMe), 1.69–1.16 (m, 12H, 6 CH_2). ^{13}C (75 MHz), δ 170.4, 170.2 (CO), 82.2, 81.9, 81.3 (C-2/C-3/C-4), 61.2, 59.6, 58.4 (6 OMe), 39.1, 29.6, 26.5 (CH_2). Anal. Calcd for $C_{20}H_{38}O_5N_2\cdot 0.5\ H_2O$: C, 54.80; H, 8.70; N, 9.13. Found: C, 54.66; H, 8.36; N, 8.85.

3. Results and discussion

3.1. Synthesis

The general procedure described for the synthesis of polyamides of *m*,*n*-type containing sugar units is based on the polycondensation in solution of diacid active esters with diamines. Two methods are reported in the literature, which differ in that the diamine is used either as trimethylsilane derivative or as free base. The PA-6Ar polyamides studied in this work have been prepared by using free HMDA in DMF as solvent in the presence of triethylamine at 60 °C. D- and L-arabinose were the starting materials for the preparation of the corresponding active pentachlorophenyl esters of 2,3,4-tri-*O*-methyl D- and L-arabinaric acids, respectively. This procedure afforded the three tri-*O*-methyl arabinaramides in moderate yields (~60%) with weight-average molecular weights within the 40,000–50,000 g mol^{-1} range and polydispersities oscillating between 1.5 and 1.7. The reaction scheme leading to such polyamides is depicted in Fig. 1.

Since the *arabino* configuration lacks C_2 symmetry axis, two orientations are feasible for the arabinaric units along an enatiomerically homogeneous PA-6Ar polyamide chain. As it is illustrated in Fig. 2, the spatial difference between the two orientations of the arabinaric unit in both PA-6DAr and PA-6LAr concerns only the arrangement of the methoxy group attached to the central carbon of the unit. In the racemic stereocopolyamide PA-6DLAr, the deviation from stereoregularity will be more pronounced since the microstructure of the chain is expected to be affected by both configurational and orientational heterogeneities. In fact, D and L-arabinaric units placed along the PA-6DLAr chain will differ from each other in the configuration of either two or the three stereocenters depending on they are inserted in the chain with the same or opposite orientation. Since no regiospecific technique was adopted for the synthesis of PA-6Ar, the three polyamides are therefore expected to be *aregic* and non-stereoregular with one, two or the three methoxy groups of the arabinaric unit randomly located on one or the other side of the polymer backbone plane.

Previous studies made on other polyamides of this type have shown that a random microstructure is generated in the polycondensation in solution of diamines and diacids involving non-centrosymmetric components. Thus, polyamides prepared from L-malic acid and hexamethylenediamine were demonstrated to be fully *aregic* on the base of the splitting observed for the α-methylene ^1H NMR signal [16]. Also, the ^{13}C NMR spectra of polyamide PA-LArLAr prepared from *O*-methylated L-arabinaric acid and 1,5-diamine-1,5-deoxy-L-arabinitol showed three signals for the carbonyl groups corresponding to the four stereochemical possibilities for the triads centered on the arabinaric unit [15]. The carbonyl signals appearing in the ^{13}C NMR spectra of PA-6LAr and PA-6DLAr are depicted in Fig. 3. In both cases, the signal appears split in four peaks with similar intensities as it should be expected for an *aregic* microstructure with similar amounts of the arabinaric units adopting each of the two possible orientations.

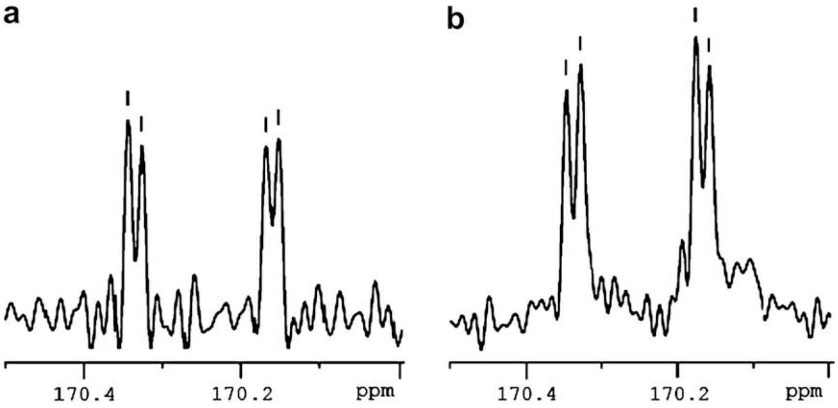

Fig. 3. Splitting of carbonyl signals in the ^{13}C NMR spectra of PA-6LAr (a) and PA-6DLAr (b).

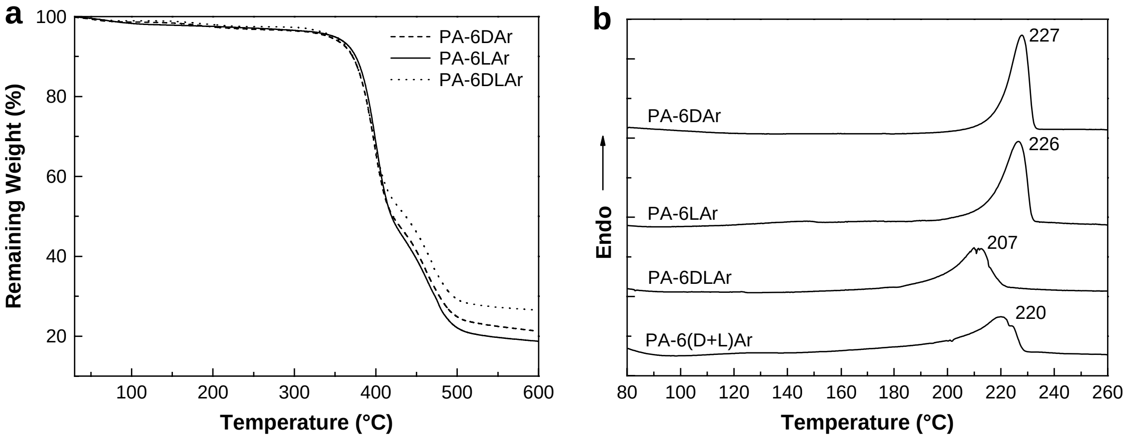

Fig. 4. TGA (a) and DSC (b) traces of PA-6Ar polyamides samples coming directly from synthesis.

Table 1
Characteristics of the polyamides used in this study.

	$[\alpha]^a$ (deg)	$T_g{}^b$ (°C)	$T_m{}^c$ (°C)	$\Delta H_m{}^c$ (J g^{-1})	$T_m{}^d$ (°C)	$\Delta H_m{}^d$ (J g^{-1})	$T_d{}^e$ (°C)	$M_w/M_n{}^f$ (kg mol^{-1})	ρ^g (g mL^{-1})
PA-6DAr	−50	97	227	48	223	43	**397**/462	40.0/23.0	1.09
PA-6LAr	+48	95	226	50	223	44	**395**/460	40.3/27.1	1.10
PA-6DLAr	0	97	207	39	205	35	**395**/470	50.2/32.2	1.05
PA-(D + L)Ar	–	96	220	39	218	40	**394**/463	–	–

[a] Specific optical rotation measured in dichloromethane-methanol (3:1), *c* 0.6.
[b] Determined by DSC at heating from quenched samples.
[c] Measured by DSC on samples from synthesis.
[d] Measured by DSC on films cast from chloroform.
[e] Measured by TGA.
[f] Determined by GPC.
[g] Determined from oriented samples by the flotation method.

3.2. Compared thermal properties

Firstly, the thermal stability of the polyarabinaramides under inert atmosphere was evaluated. As it is seen in Fig. 4a, the TGA traces produced by the three polyamides are practically undistinguishable. A two-stage decomposition process with maximum rate decomposition temperatures at ~395 and ~460 °C and leaving around 20–30% of carbonaceous residue was observed for the three compounds. The small differences detected among them can be considered to be well within the experimental range of error. The weight loss observed below 200 °C, which amounts around 3% of the initial mass, is attributed to the loose of absorbed water. The onset decomposition temperature (defined as that at which 5% of initial weight is lost) is around 300 °C. These data lead us to conclude therefore that the heat resistance of PA-6Ar polyamides is high and that their thermal stability is not appreciably affected by configurational effects.

The DSC traces produced by films of PA-6Ar polyamides prepared by casting from $CHCl_3$ are compared in Fig. 4b. The thermograms of the three compounds display well-defined endothermic peaks characteristic of melting. As it should be expected, PA-6DAr and PA-6LAr display almost identical melting temperatures and enthalpies whereas significant lower values are observed for the racemic copolyamide PA-6DLAr. Similar results were obtained in the DSC analysis of films obtained by casting from formic acid. The DSC analysis of the powder of synthesis of these polyamides revealed that such samples are more crystalline and display slightly higher melting temperatures than films; such a behavior is widespread found in polyamides indicating that crystallization is favored by precipitation. The thermal parameters afforded by DSC

Table 2
Observed and calculated X-ray spacings (Å) for polyamides PA-6Ar.

Observed								Calculated^c	
PA-6DAr	PA-6LAr	PA-6DLAr	PA-6(D + L)Ar	PA-6LAr				*hkl*	d_{hkl}
Powder patterns				Film^a	Fiber	Mat^b	Lamella^b		
10.72w	10.72w	10.83w	10.72w	10.64w	11.0s	11.0s		002	11.0
8.44s	8.44s	8.35s	8.44s	8.38s	8.17s	8.20s	8.17	020	8.26
6.69m	6.65m	6.60m	6.56m	6.65w	6.65m	6.65m		022	6.62
5.48w	5.48w	5.51w	5.48w	5.72w	5.55w	5.53w		023	5.50
4.73s	4.73s	4.65s	4.73s	4.63s	4.63s	4.63s	4.63	110	4.68
4.37w	4.37w	4.37w	4.37w	4.35w	4.30w	4.35w		112	4.31
3.75w	3.75w	3.75w	3.67w	3.84w	3.85w	3.79w		025	3.90
							2.45	200	2.44

[a] Cast from formic acid.
[b] Lamellae crystallized in glycerin at 130 °C.
[c] Spacings calculated for a rhombic lattice of parameters: $a = 4.88$ Å, $b = 16.52$ Å, $c = 22.1$ Å, $\alpha = \beta = \gamma = 90°$;, which contains four repeating units per unit cell. The density calculated for this structure is 1.125 g mL^{-1}.

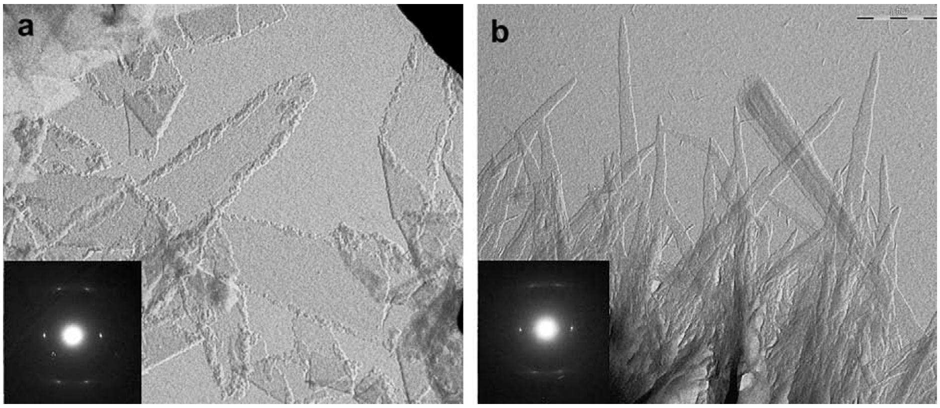

Fig. 5. Lamellar crystals of PA-6LAr (a) and PA-6DLAr (b) grown in glycerin at 130 °C. Insets: Respective electron diffraction patterns. The scale bar shown in b) is applicable to both pictures.

together with TGA data are compared in Table 1. What is really relevant of the DSC analysis is the indication that the two polyamides PA-6DAr and PA-6LAr are highly crystalline in spite of not being stereoregular. The ability to crystallize is even retained in the case of racemic PA-6DLAr, although in this system both crystallinity and crystal perfection slightly decreased as the logical consequence of the additional structural distortion that is introduced by configurational heterogeneity.

3.3. *Crystal morphology and structure*

The crystal structure of PA-6Ar polyamides was examined by X-ray and electron diffraction from powders, films, fibers and lamellar crystals, and the diffraction data obtained in this study are collected in Table 2. The X-ray diffraction patterns recorded from powdered samples coming directly from synthesis (not shown) of both enantiomerically pure and racemic polyarabinaramides consisted of several sharp rings indicative of crystalline material, which is in full agreement with the DSC data discussed above. The patterns for the three polyamides displayed the same features with reflections being similar in both spacings and intensities, which strongly suggests that the same crystal structure is shared by the three compounds. Crystallization of PA-6LAr at 130 °C from a dilute solution of the polymer in glycerin rendered the lamellar crystals shown in Fig. 5a. They are flat elongated lamellae with a thickness of about 80 Å and displaying massive overgrowing on the edges. The electron diffraction pattern produced by these crystals contain two pairs of reflections at 8.17 Å and 4.63 Å consistent with the occurrence of a rectangular lattice of about 8.2 Å and 4.9 Å oriented with the *c*-axis (chain axis) parallel to the direction of the electron beam. These two reflections appear in the powder patterns as two highly intense rings at 8.4 Å and 4.7 Å. Crystallization of PA-6DLAr

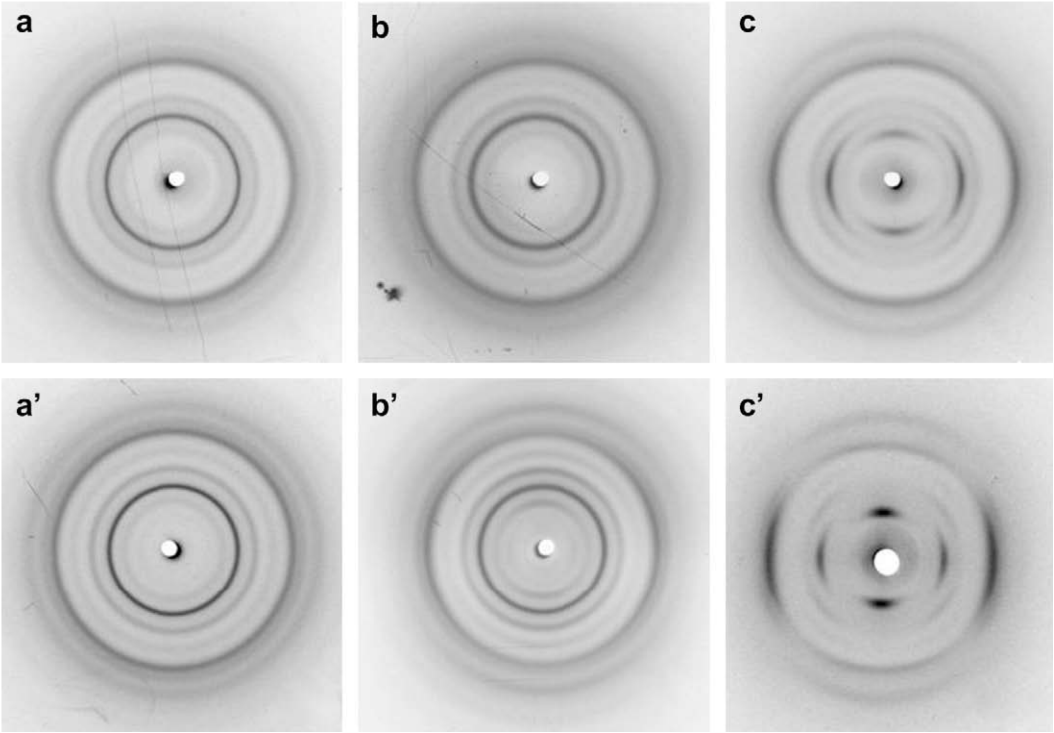

Fig. 6. WAXS patterns of PA-6LAr (top) and PA-6DLAr (bottom). a,a′) Film cast from formic acid; b,b′) Sediment of lamellar crystals obtained by crystallization from diluted solution in glycerin; c, c′) Stretched fiber.

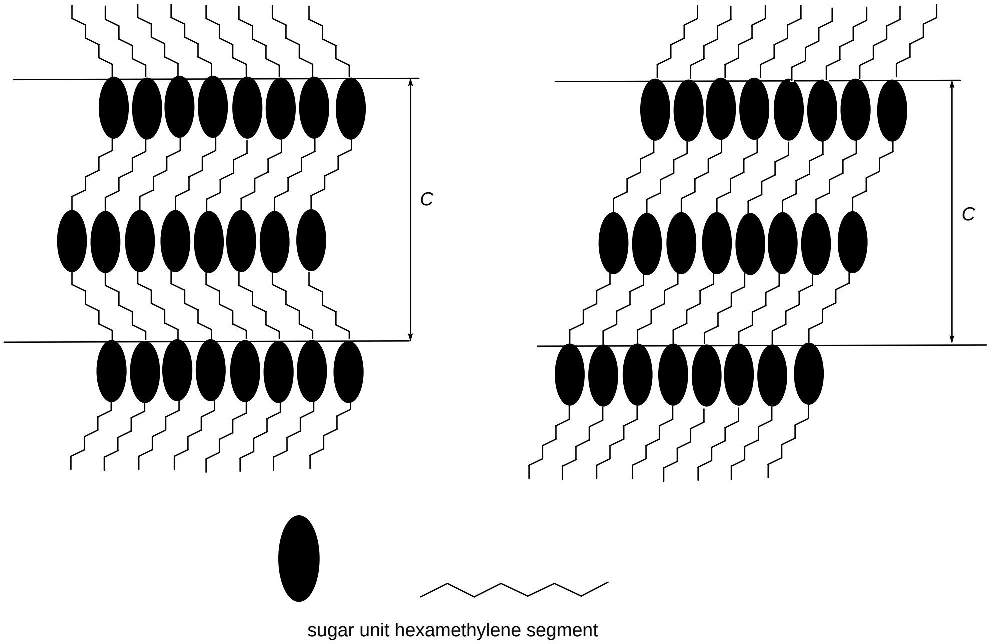

Fig. 7. Scheme of possible molecular arrangements of PA-6Ar chains in the crystal lattice.

carried out under similar conditions afforded also elongated lamellar crystals of similar thickness but without occurrence of visible edge overgrowing (Fig. 5b). The electron diffraction patterns produced by these crystals is practically undistinguishable from that obtained from PA-6LAr crystals indicating that the same lattice must be adopted by the two polymers upon crystallization from dilute solution.

The evaporation of a solution of polyarabinaramide in formic acid at room temperature led to highly birefringent thin films displaying an appearance that changed from a well-defined spherulitic texture for PA-6DLAr to a homogeneous grainy texture for PA-6LAr. Such a difference in texture between enantiomerically pure and racemic polyarabinaramides was also appreciated in films

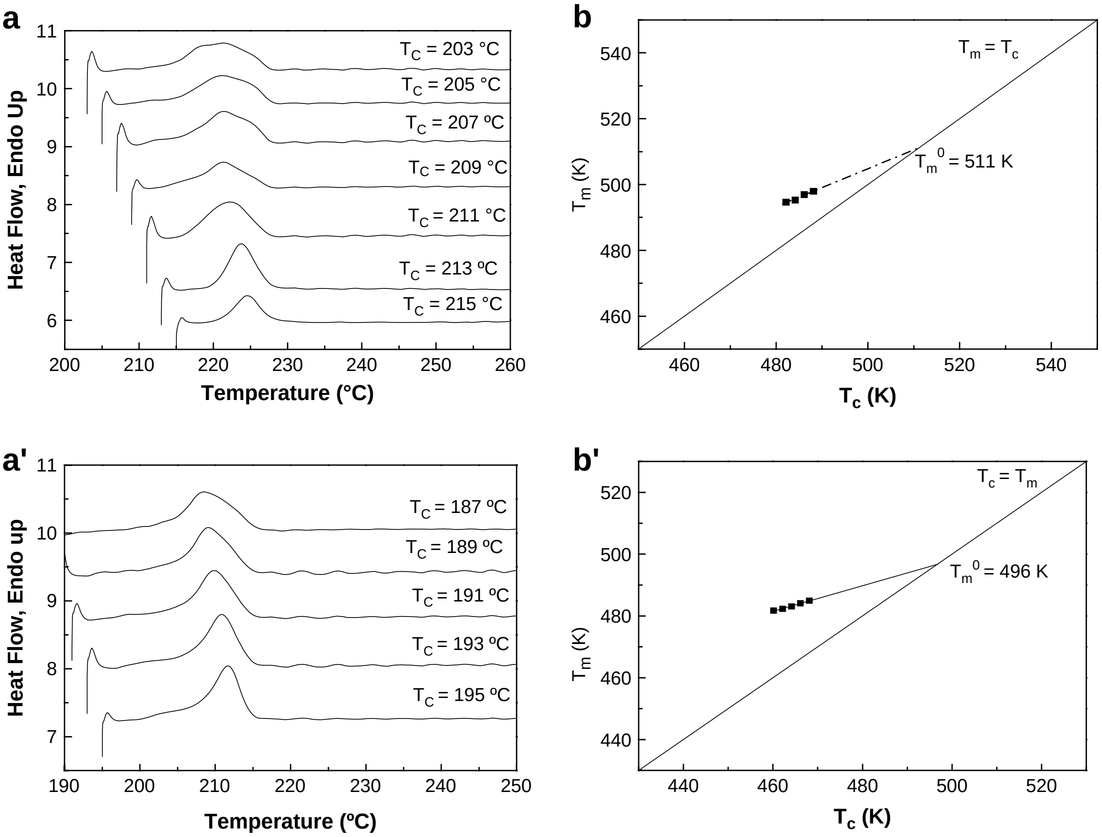

Fig. 8. Heat flow *vs* temperature (a and a′) at a heating rate of 10 °C min^{-1} crystallized at the indicated temperatures (a and a′) and plot of the resulting T_m against T_c (b and b′) for PA-6LAr (top) and PA-6DLAr (bottom).

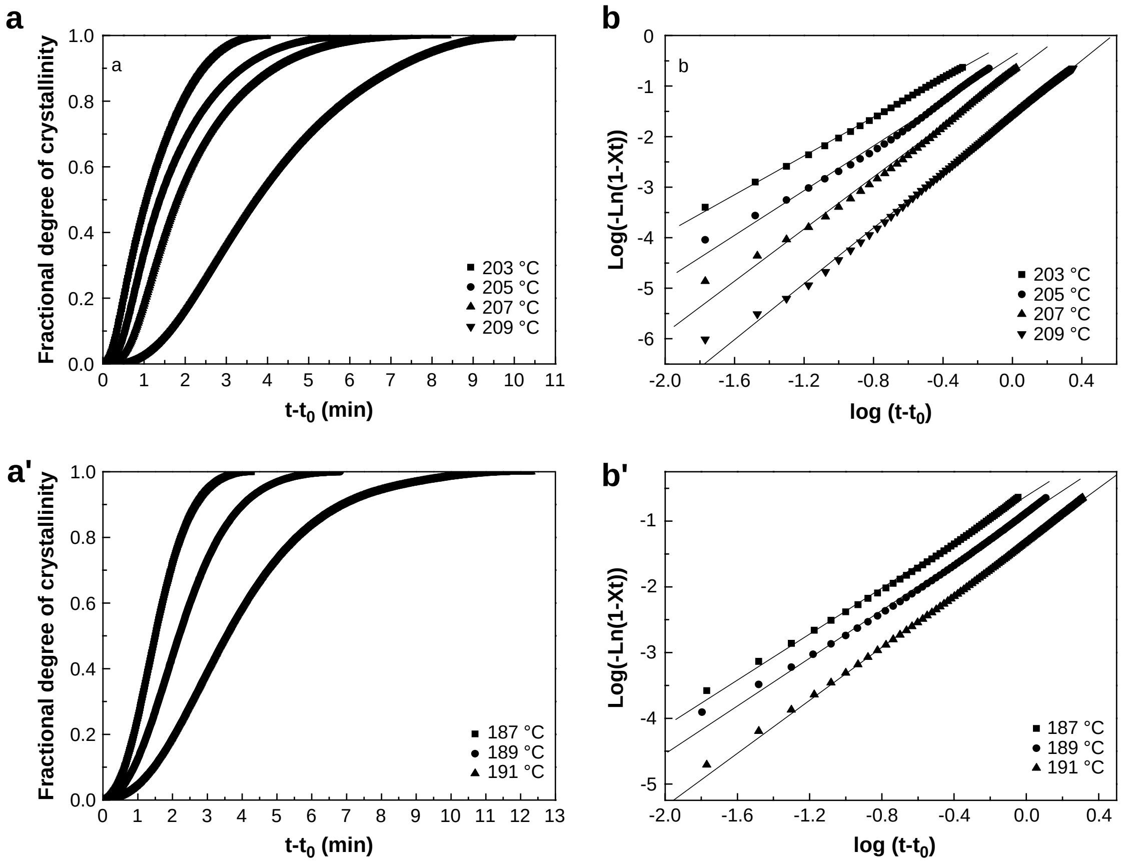

Fig. 9. Fractional degree of crystallinity *vs* time (a and a′) and plot of log(−ln(1 − *Xt*)) *vs* log (*t* − t_0) (b and b′) for isothermal crystallization of PA-6LAr (top) and PA-6DLAr (bottom).

cast from other solvents as $CHCl_3$ or DMF, and it is interpreted to be due to the poorer solubility of the optically pure polyamides which cause a much higher nucleation density upon evaporation. On the other hand, the appearance displayed by films crystallized from the melt is quite similar: they all consist of a fan-like type texture with clear indications of the occurrence of spherulitic structures. The powder X-ray diffraction patterns obtained from films of PA-6LAr and PA-6DLAr prepared by casting from formic acid are compared in Fig. 6 (the pattern obtained from PA-6DAr, not included, is almost identical to that produced by PA-6LAr). It can be seen that the two polyamides produce well-definite scattering such as it should be expected for crystalline materials and that the texture differences observed by POM are not reflected in these patterns. The patterns recorded from the sediment of the crystals of PA-6LAr and PA-6DLAr isothermally grown from solution of the polymer in glycerin are compared in Fig. 6. Spacings and intensities of the reflections appearing in all these patterns are very similar giving support to previous indication that the three polyamides seem to adopt the same crystal structure. Further support to this fact is provided by comparing the fiber diffraction patterns shown in Fig. 6; the reflections displayed by these patterns are almost identical in spacing, orientation and relative intensity, the only observable difference among them being the breath of the spots which is solely determined by the degree of orientation attained in each sample upon stretching.

All the reflections observed in the diffraction patterns of the different analyzed samples could be indexed on the basis of a rhombic crystal lattice with parameters $a = 4.88$ Å, $b = 16.52$ Å, $c = 22.1$ Å, $\alpha = \beta = \gamma = 90°$. The density calculated for this structure is 1.125 g mL^{-1}, in good agreement with the value of 1.10 g mL^{-1} experimentally found. All observed and calculated spacings with their corresponding indexes are listed in Table 2. Some relevant features of this structure are:

a) The side-by-side arrangement adopted by the polyamide chains seems to be similar to that described for the γ-form of nylon 6,5 [17], *i.e.* chains arranged in sheets with hydrogen bonds intermolecularly set between amide groups; such arrangement implies however a twisting in the arabinaric unit backbone for HN–NH and CO–CO segment lengths of the interlocked neighboring chains are able to fit to each other.
b) According to previous studies carried out on polyamides containing tartaric acid units [18], the structure is thought to be stratified with the arabinaric units in skew conformation and the hexamethylene segments in all trans conformation arranged in alternating layers. The axial repeat of the structure is 11.05 Å, which is about 5 Å shorter than the length calculated for the repeating unit of the polyamide 6,5 in fully extended conformation. Such a shortening would be the result of both the contraction of the sugar moiety and the tilting of the polymethylene segment respect to the *c*-axis of the crystal.
c) Density calculations lead to a lattice containing four repeating units in the unit cell. This implies a staggered array of successive hydrogen-bonded sheets so that they are displaced to each other by 1/2*a*. Such arrangement is usual in nylons [19] and it is known to arise as a result of the favorable methylene–methylene and amide–amide dipole–dipole interactions taking place between adjacent sheets. In the present case, such arrangement seems to be particularly appropriate since it will make possible the comfortable accommodation of the three methoxy side groups protruding from the arabinaric unit.

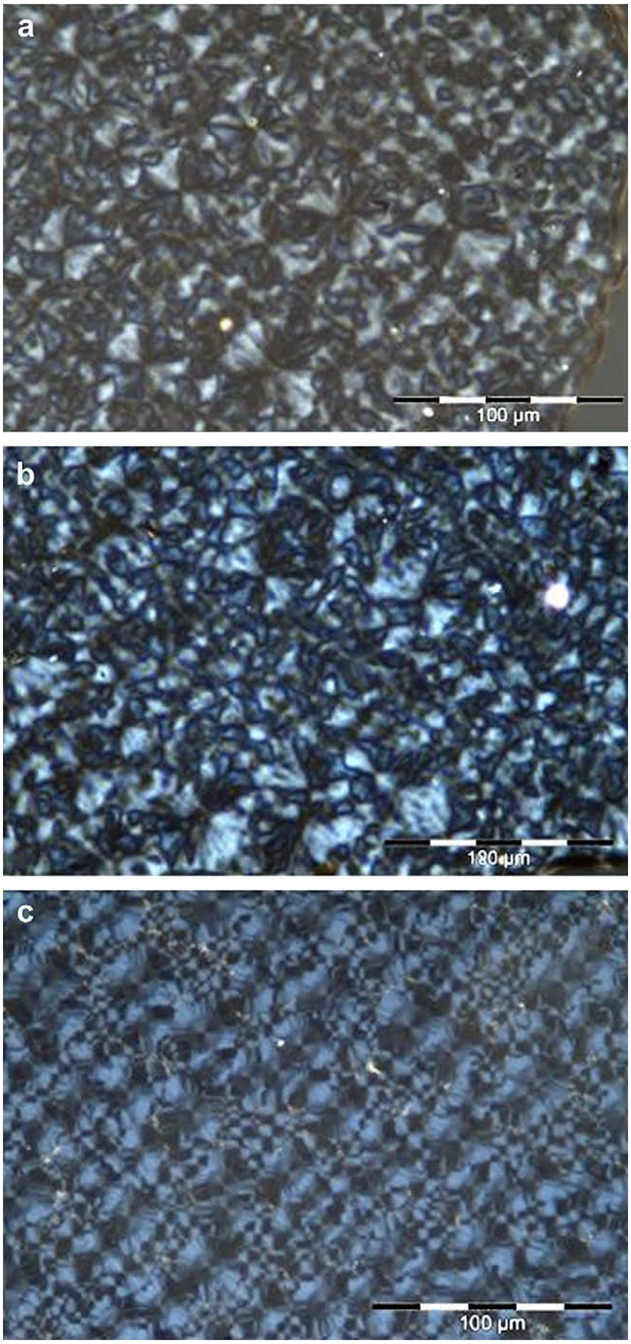

Fig. 10. Polarizing optical micrographs of thin films of PA-6Ar crystallized from the melt at the indicated temperatures: (a) PA-6DAr (195 °C); (b) and PA-6LAr (195 °C); (c) PA-6DLAr (180 °C).

d) Neither the configuration nor the orientation of the arabinaric units along the polyamide chain appears to have decisive influence on the crystal structure. The molecular organization in the crystal lattice seems to be determined by efficient interlocking of the arabinaric units allowing complete and comfortable hydrogen-bonding between them and a closely side-by-side packing of the polymethylene segments. No data are available however to know in detail what is the conformation of the polyamide chains and how it is modified by mismatching in orientation and/or configuration of the interlocked arabinaric units. Modeling and simulation studies, which are out of the scope of this work, are under course to elucidate this issue.

A crude scheme of the structure of PA-6Ar, which is inspired in previous studies carried out on polytartaramides [18] and that is supported by the experimental data collected in this work, is depicted in Fig. 7 to illustrate the most relevant features of the structure.

3.4. Compared isothermal crystallization

Since all the three stereoisomeric PA-6Ar polyamides are able to crystallize from the melt, their isothermal crystallization kinetics could be comparatively studied. The DSC heating traces produced by PA-6LAr and PA-6DLAr isothermally crystallized at different temperatures are shown in Fig. 8 (a and a′). The plot of T_m *vs* T_c resulted in straight lines that extrapolated to $T_\mathrm{m} = T_\mathrm{c}$ rendered the respective equilibrium melting temperatures (Fig. 8b and b′), which were found to be 238 and 233 °C, respectively. The same treatment applied to PA-6DAr yielded results practically undistinguishable from those obtained for its enantiomorph PA-6LAr with an equilibrium T_m of 239 °C.

The crystallization kinetics was examined at different crystallization temperatures by applying the Avrami's approach [20] and following recently published methodologies specifically designed for the analysis of polymeric systems [21,22]. Fractional crystallinity as a function of time and the corresponding logarithmic Avrami plots for a relative crystallinity range of 0.2–0.8 are plotted in Fig. 9 for PA-6LAr and PA-6DLAr, and both experimental and calculated crystallization parameters are given in Table 3 for the three studied polyamides. For comparison purposes, the inverse of the experimental half-crystallization time as a function of T_c has been plotted in Fig. 11 for all the systems under study. As expected, for a given polyamide the crystallization rate decreased with crystallization temperature as it is clearly reflected in the regular increasing of crystallization-half times that is observed for increasing values of T_c. Crystallizations of PA-6LAr and PA-6DAr were compared within the temperature range of 203–209 °C; the kinetic parameters resulting for the two polyamides were almost coincident for the whole set of essayed temperatures. Unfortunately, PA-6DLAr could not be crystallized at the same temperature which prevented a similar comparative kinetic study. Nevertheless, if available data are compared taking into account the temperature at which each polyamide was crystallized, it is acceptable to conclude that crystallization of the racemic PA-6DLAr proceeded at much lower rate.

Avrami exponent values were found to oscillate between 2 and 3 with values going down at crystallization temperatures decrease. The highly uniform size and texture displayed by POM pictures (Fig. 10) indicated that crystallization occurred instantaneously with a morphology displaying some spherulitic reminiscences but with features recognizable from a smectic mesophase. This in agreement with the rather low value found for *n* and their parallel dependence on temperature, and also with the type of crystal structure thought for these systems, in which a perfect packing of molecules is intrinsically unfeasible.

3.5. Study of the racemic mixture of PA-6(D + L)Ar

The interesting fact that some enantiomorph pairs of sugar-derived polyamides, specifically poly(hexamethylene di-*O*-methyl tartaramide)s (PA-6LThr) are known to be able to form stereocomplexes with distinctive structure and properties [23], led us to investigate this issue in the present case. Thus the thermal and structural behavior of the stoichiometric mixture of polyamides PA-6DAr and PA-6LAr, called henceforth PA-6(D + L)Ar, was examined and results arisen from this study were compared to those obtained for the enantiomerically pure polyamides. The racemic mixture was prepared by dissolving a mixture of the two optically

Table 3
Isothermal crystallization of polyarabinaramides.

	T_c (°;C)[a]	ΔH_c (J g^{-1})[a]	T_m (°C)[b]	ΔH_m (J g^{-1})[b]	t_o (min)[c]	$t_{1/2}$ (min)[d]	n[e]	k (min^{-n})[e]	$t_{1/2}$ (min)[f]
PA-6LAr	203	20.6	221.3	25.6	0.35	1.05	1.91	0.70	0.90
PA-6LAr	205	19.6	221.6	22.4	0.40	1.40	2.21	0.11	1.30
PA-6LAr	207	16.6	221.5	22.8	0.63	1.84	2.57	0.012	1.68
PA-6LAr	209	11.8	221.3	19.4	1.18	3.77	2.76	2.0×10^{-05}	3.31
PA-6DAr	203	21.3	221.1	25.6	0.36	0.83	2.03	1.21	0.79
PA-6DAr	205	19.9	220.5	21.0	0.41	1.41	2.34	0.05	1.41
PA-6DAr	207	14.4	221.3	23.1	0.68	1.97	2.46	6.6×10^{-03}	1.94
PA-6DAr	209	13.7	221.7	22.1	1.35	4.20	2.77	1.9×10^{-05}	3.60
PA-6DLAr	189	20.7	209.1	26.1	0.46	2.22	1.81	0.021	2.57
PA-6DLAr	191	17.6	209.9	23.9	0.60	3.60	2.01	2.4×10^{-03}	3.72
PA-6(D + L)Ar	189	26.6	214.7	30.5	0.51	0.93	2.22	0.24	1.12
PA-6(D + L)Ar	191	24.3	215.6	29.5	0.66	1.05	2.23	0.21	1.15
PA-6(D + L)Ar	203	15.5	219.8	15.9	1.80	4.99	2.35	2.6×10^{-04}	3.91

[a] Crystallization temperature and enthalpy.
[b] Melting temperature and enthalpy.
[c] Crystallization onset time.
[d] Crystallization half-time determined experimentally.
[e] Avrami parameters.
[f] Crystallization half-time calculated by Avrami, $t_{1/2} = (\mathrm{Ln}\ 2/k)^{1/n}$.

pure polyamides in $CHCl_3$; films were obtained by evaporating the solution to dryness at room temperature and powdered samples were obtained by precipitation with diethyl ether. The DSC heating traces obtained from this mixture were very similar to those recorded from the racemic copolyamide PA-6DLAr with a melting peak at lower temperature and an enthalpy slightly lower than those obtained for the individual components. The wide angle X-ray diffraction analysis of the powder produced a pattern hardly distinguishable from those obtained from the separated components. All these data are compared in Tables 1 and 2 showing that no stereospecific complex seems to be formed by the PA-6(D + L)Ar mixture.

The only differences between PA-6DAr or PA-6LAr and their stoichiomeric mixture that deserve attention were those observed in the crystallization kinetics analysis. Fortunately, PA-6(D + L)Ar could be isothermally crystallized over a wide range of temperatures so that a straight comparison either with the homopolyamides or with the copolyamide could be made. Comparison of such data (Table 3 and Fig. 11) indicates that PA-6(D + L)Ar crystallized faster than the copolyamide PA-6DLAr but much slower than the optically pure components. This behavior is similar to that reported for the pair of enantiomeric PA-6(D + L)Thr polyamides which is proved to form a stereospecific complex melting 20 °C higher than both PA-6DThr and PA-6LThr [24].

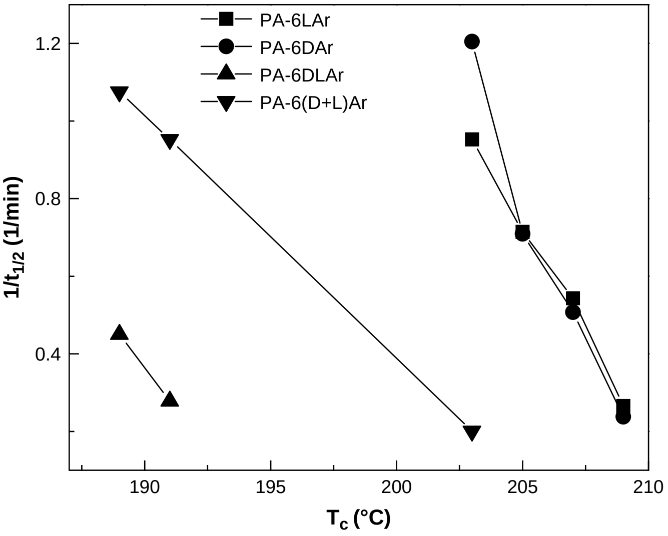

Fig. 11. Inverse of half-crystallization time *vs* T_c for the four systems under study.

4. Conclusions

A comparative experimental study embracing crystal structure and crystallization kinetics has been carried out on stereoisomeric polyarabinaramides with an *aregic* microstructure and different enantiomeric composition. The first and general conclusion drawn from this study is that all these polyamides are semicrystalline in spite of being non-stereoregular, *i.e.* neither orientation isomerism nor configurational heterogeneities prevent them to crystallize. Secondly, it can be concluded that heterogeneity in configuration does not affect significantly to either their thermal properties or their crystal structure. All they crystallize in a rhombic lattice made of hydrogen-bonded sheets in which the sugar moiety is in a skewed arrangement and the hexamethylene segment is significantly tilted in order to attain a close molecular packing. They display some differences, however, concerning crystallization kinetics, with the racemic copolyamide crystallizing at much lower rate than optically homogeneous polyamides. The thermal properties and crystal structure of the stoichiometric mixture of the two enantiomerically pure polyamides do not distinguish from its components revealing that, at difference with other previously sugar-containing polyamides, not stereocomplex is formed in this system.

Acknowledgements

Financial support for this work was provided by CICYT (Spain) with grant MAT2006-13209-C02. Authors are indebted to AGAUR and MEC for the Ph.D. grants awarded to Carlos E. Fernández and Romina Marín, respectively.

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