

Hairy-rod random copoly(β ,L-aspartate)s containing alkyl and benzyl side groups

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Received 1 August 2002; received in revised form 8 October 2002; accepted 18 October 2002

Abstract

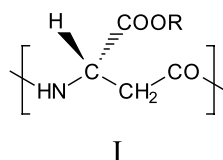
Hairy random copoly(β ,L-aspartate)s were prepared by anionic ring opening polymerization of mixtures of (*S*)-4-octadecoxycarbonyl and (*S*)-4-benzyloxycarbonyl 2-azetidinones at 3:1, 1:1 and 1:3 molar ratios. The three resulting copolymers had molar ratios of octadecyl to benzyl units of 68:32, 44:56 and 12:88, respectively. They all were found to adopt the rigid α -helix-like conformation characteristic of poly(β ,L-aspartate)s, but only the first one displayed crystallization of the alkyl side chains. This copolymer showed thermochromic behavior with color changes taking place when heated above the side chain melting temperature. These results evidenced the ability of the benzyl group to be accommodated within the layered structures of comb-like poly(β ,L-aspartate)s and to modify the temperature range in which chromatic changes are observed in these systems.

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Keywords: Copolymers; Aspartates; Side groups

1. Introduction

Poly(α -alkyl β ,L-aspartate)s (PAALA) (I) are poly(β -peptide)s able to adopt rod-like helical conformations with features similar to the familiar α -helix characteristic of poly(α -amino acid)s [1–4].



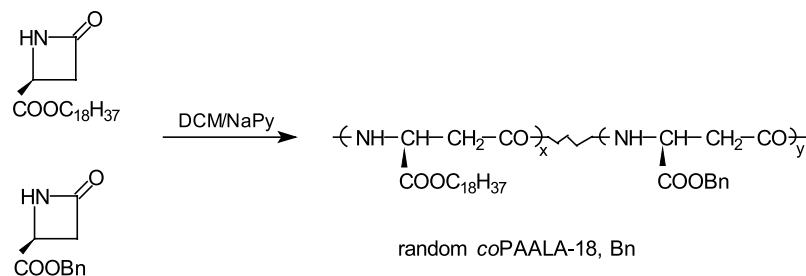
The most frequent conformational arrangements present in these polymers are the 13/4 and the 4/1 helices. Concentrated solutions of poly(α -alkyl β ,L-aspartate)s in halogenated solvents are known to form cholesteric mesophases [5], and the structure that they adopt in the solid state strongly depends on the length of the alkyl side chain. Members bearing short alkyl side groups (C_1 to C_5) crystallize in three-dimensional hexagonal or tetragonal

lattices [6], whereas those with long linear alkyl groups become organized in a biphasic layered structure (phase A) in which the layers made of 13/4 helices are separated by the crystallized polymethylene side chains [7].

Melting of the side chains of comb-like poly(α -alkyl β ,L-aspartate)s happens at low temperatures inducing the transition of phase A into the mesophase B, which presumably has a cholesteric structure. In this phase, the molten side chains will play the role of the solvent in a lyotropic system. Heating at higher temperatures leads to a third phase (C), in which the layered arrangement is abandoned while the main chains retain the helical conformation [7]. Upon interaction with polarized light, striking color changes covering practically the whole visible chromatic range, take place at definite temperatures within the domain of existence of mesophase B [8]. The response is instantaneous, fully reversible and highly sensitive to temperature. Such a thermochromic behavior may be of benefit in the development of thermosensors to be used under temperatures near to physiological conditions.

Copoly(α ,L-glutamate)s [9–11] and copoly(L-aspartate)s [12,13] were previously investigated in connection with their mesogenic and chromatic properties. Specifically, copoly(β ,L-aspartate)s containing short and long alkyl side

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Scheme 1.

chains were shown to form solid state structures and mesophases similar to those adopted by their parent comb-like homopolymers [13]. Since the phase transition temperatures in the copolymers vary with the comonomer composition, the thermochromic response of comb-like poly(β ,L-aspartate)s is susceptible of being modified by copolymerization.

In this paper, we wish to report on poly(β ,L-aspartate) copolymers bearing octadecyl and benzyl side groups, called *co*PAALA-18,Bn henceforth. The homopolymer poly(α -octadecyl β ,L-aspartate), called PAALA-18, is known to adopt the layered structure typical of comb-like polymers with layers separated 3.1 nm and the alkyl side chains partially crystallized with about 8–9 methylenes being included in the crystalline core [7]. Although the structure of the homopolymer poly(α -benzyl β ,L-aspartate) (PABLA) has not been reported yet, it is reasonable to assume that it will take up the type of crystalline arrangement adopted by poly(β ,L-aspartate)s carrying short alkyl side groups. The partial replacement of the octadecyl group by the benzyl group is expected therefore to change the phase transition temperatures of the homopolymer, and consequently its thermochromic behavior. The specific objective intended in this study is to evaluate the effect of the benzyl group on the structure and properties of comb-like PAALA-18, and to see how it compares in this regard with the butyl group previously investigated by us.

2. Experimental

The optically pure (*S*)-4-benzyloxycarbonyl-2-azetidinone was obtained from commercial L-aspartic acid [14]. (*S*)-octadecyloxycarbonyl-2-azetidinone was prepared by transesterification of the former with stearyl alcohol [15]. The random copolymers were prepared as following: Under a stringent nitrogen atmosphere and vigorous stirring, the mixture of the two β -lactams at the chosen ratio was dissolved in dichloromethane to have a final monomer concentration of 8%(w/w). Sodium pyrrolidone was then added to have a 4%-mole concentration of catalyst. Polymerization was left to proceed at room temperature for 48 h, after which, the reaction mixture was diluted with fresh solvent and precipitated with methanol. Purification was accomplished by repeated precipitation and the

copolymer was recovered by centrifugation and stored under vacuum.

Densities were measured by the flotation method in aqueous KBr–water mixtures. Dichroic infrared spectra (DIR) were registered on a Perkin–Elmer 2000 spectrophotometer provided with a gold wire polarizer. NMR spectra were recorded in solution at room temperature on an AMX-300 Bruker instrument operating at 300.1 and 75.5 MHz for ^1H and ^{13}C , respectively. Samples were dissolved in deuterated chloroform–trifluoroacetic acid mixtures containing a small amount of tetramethylsilane as internal reference. Calorimetric measurements were carried out at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under a nitrogen atmosphere on a Pyris I Perkin–Elmer DSC instrument calibrated with indium. Thermogravimetric analyses were performed at a heating rate of $20\text{ }^\circ\text{C min}^{-1}$ on a Perkin–Elmer TGA 6 thermobalance. X-ray diffraction patterns were recorded on flat photographic films in a Statton-type camera using nickel-filtered $\text{Cu K}\alpha$ radiation. Optical microscopy was carried out in a Nikon Labophot microscope provided with a heating stage Mettler FP-86. All films were prepared by casting from chloroform and, if needed, uniaxially oriented by mechanical stretching.

3. Results and discussion

The synthesis procedure used in the preparation of

Table 1
Polymerization results

(C ₁₈ /Bn) composition		Yield (%)	$[\eta]^a$ (dl g ⁻¹)	ρ (g ml ⁻¹)
Feed ^b	Polymer ^c			
100:0	100:0	86	2.67	1.030
75:25	68:32	66	3.29	1.037
50:50	44:56	52	3.12	1.069
25:75	12:88	74	3.78	1.090
0:100	0:100	95	3.42	1.105

^a Intrinsic viscosity measured in CHCl_3/DCA (2:1) mixture except for 0:100 ratio, which was measured in pure DCA.

^b Molar ratio of (*S*)-4-octadecyloxycarbonyl to (*S*)-4-benzyloxycarbonyl-2-azetidinone in the feed.

^c Molar ratio of α -octadecyl to α -benzyl β ,L-aspartate units in the resulting copolymer calculated on the basis of ^1H NMR data with an assumable error of $\pm 0.5\%$.

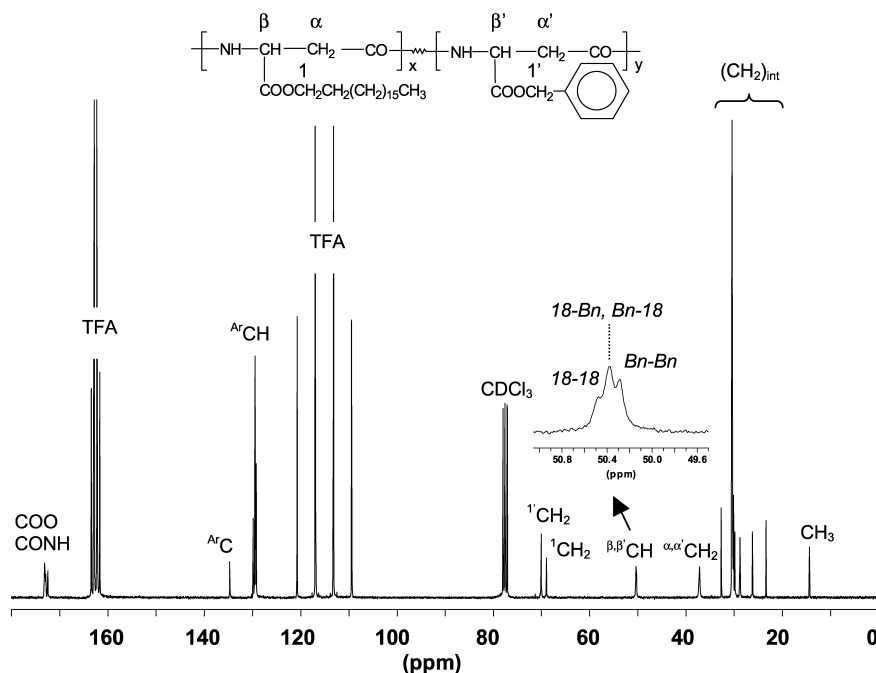


Fig. 1. ^{13}C NMR of *co*PAALA-18,Bn (44:56). Inset: the main chain methine signal used for the determination of dyads content.

*co*PAALA-18,Bn is depicted in Scheme 1 and the results obtained are summarized in Table 1. Pure (*S*)-4-octadecoxycarbonyl-2-azetidinone and (*S*)-4-benzoyloxycarbonyl-2-azetidinone, as well as their 3:1, 1:1 and 1:3 mixtures, were polymerized to render, respectively, the two parent homopolymers and the corresponding copolymers in 50–95% yields. The polymers showed intrinsic viscosities between 2.7 and 3.8 dl g⁻¹. By comparison with data previously reported for PAALA-18 [7], the molecular weights of the *co*PAALA-18,Bn are estimated to be higher than 100,000.

The chemical constitution expected for the copolymers was assessed by both ^1H and ^{13}C NMR spectroscopy. No racemization is expected to take place upon copolymerization since PAALA-18 and PABLA homopolymers obtained under similar conditions were found to be optically pure. Copolymer compositions were determined by relating the integrated areas of the peaks arising from the methylene protons in the alkyl and benzyl side groups. Results from this analysis revealed that the alkoxycarbonyl β -lactam

entered in the growing copolymer chain at a lower rate than the benzoyloxycarbonyl β -lactam. This result is contrary to that found previously in the synthesis of *co*PAALA-18,4 [13], where the composition of the resulting copolymer essentially coincided with the composition of the feeding mixture. The signal at 50.4 ppm arising from the main chain methine carbon in the ^{13}C NMR spectra (Fig. 1), was used to characterize the microstructure of the copolymer. This signal is resolved in three peaks attributable to 18-18, 18-Bn/Bn-18 and Bn-Bn compositional dyads. By lorentzian deconvolution of this signal the %molar ratios found for the three dyads were 18.2, 50.2 and 31.6, respectively, which are very similar to those theoretically expected for the copolymer *co*PAALA-18,Bn (44:56) with a random microstructure (19.4, 49.3 and 31.4). These results led to conclude that the *co*PAALA-18,Bn have a random distribution of the two comonomer units along the polymer chain.

The decomposition temperatures of *co*PAALA-18,Bn evaluated by TGA are given in Table 2 indicating that all of

Table 2
Thermal properties and powder X-ray spacings of *co*PAALA-18,Bn

Polymer (C ₁₈ /Bn)	T_m^a (°C)	ΔH^a (kcal mol ⁻¹ C ₁₈ ⁻¹)	T_d^b (°C)	d_{hkl} (nm) ^c
100:0	45–60	15	295	3.10 (vs); 1.55 (m) 0.42 (s)
68:32	35–50	4	335	3.0 (vs); 1.51 (s); 10.40 (w). 0.45 (m); 0.42 (s)
44:56	n.o.	n.o.	305	2.90 (vs); 1.40 (m) 0.45 (s); 0.40 (m)
12:88	n.o.	n.o.	280	2.72 (vs); 12.5 (s) 0.45 (vs) 0.40 (m)
0:100	n.o.	n.o.	330	1.60 (s); 1.25 (s) 0.48 (s); 0.44 (s)

^a Melting temperatures and enthalpies measured by DSC on pristine samples at a heating rate of 10 °C min⁻¹; (n.o.: not observed).

^b Decomposition temperature defined as that corresponding to the most intense peak appearing on the derivative curve of the TGA trace.

^c Visual estimates of intensities denoted as vs (very strong), s (strong), m (medium), w (weak).

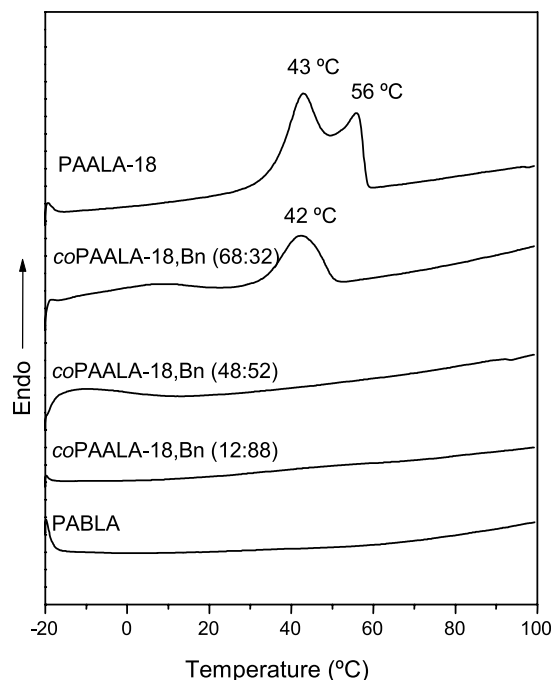


Fig. 2. Compared heating traces for PAALA-18, PABLA and *co*PAALA-18,Bn copolymers with the indicated compositions.

them are stable up to near 300 °C. As previously reported for PAALA-18, decomposition of PAALA-*n* is known to take place in two steps, the first corresponding to an intramolecular imidation reaction implying the removal of the alkyl side group and subsequent volatilization of the formed alcohol, and the second being related to unspecific main chain scissions.

The DSC heating traces of all these polymers displayed strong endothermic peaks in the temperature region of 280–350 °C, which according to TGA observations, must be attributed to a simultaneous melting–decomposition process. What it is most interesting in this context, however, is the occurrence of thermal transitions at low temperatures, i.e. below 150 °C. The DSC traces region recorded in the –20 to 100 °C range from *co*PAALA-18,Bn and the two parent homopolymers are depicted in Fig. 2. The endothermic double peak observed for PAALA-18 arises from the melting of the interlayer crystallites made up of octadecyl side chains. *co*PAALA-18,Bn (68:32) was the only copolymer showing heat absorption attributable to side chain melting. This behavior clearly differs from that observed for *co*PAALA-18,4 copolymers which are known to display side chain crystallization for contents in octadecyl units as low as 50% [13].

The structure of *co*PAALA-18,Bn was investigated by DIR and X-ray diffraction using uniaxially stretched films. Characteristic amide A, amide B, amide I and amide II bands appeared in the infrared spectrum (Fig. 3) displaying parallel dichroism consistent with the presence of 13/4 helices aligned parallel to the stretching direction [7]. Note that amide I and amide II bands in the infrared spectra of

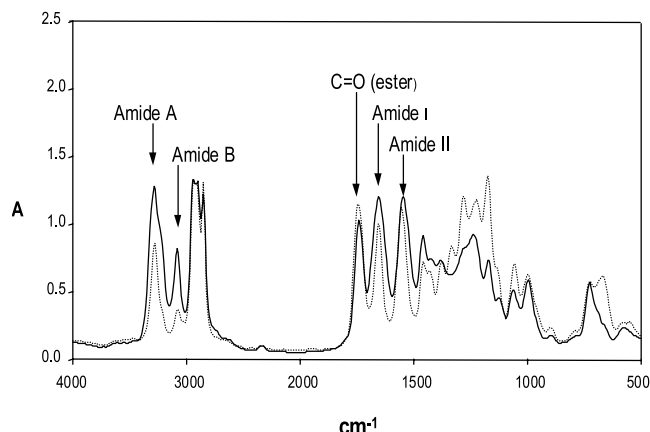


Fig. 3. Polarized infrared spectra of *co*PAALA-18,Bn (68:32) recorded with the electric vector of the polarized radiation parallel (solid line) and perpendicular (dotted line) to the orientation axis of the copolymer film.

poly(α -amino acid)s in the conventional α -helix conformation display parallel and perpendicular dichroism, respectively. The anomalous dichroic behavior observed for the 13/4 helix has been investigated in detail and it is attributed to the fact that the amide group is less inclined in this conformation than in the α -helix conformation [16]. All the *co*PAALA-18,Bn showed similar dichroic behavior indicating that the helical arrangement is retained whichever is the copolymer composition.

X-ray diffraction produced the oriented patterns shown in Fig. 4 and the spacings measured on them are compared in Table 2. The pattern of PAALA-18 clearly corresponds to the phase A of this polymer, which is characterized by a layer period of 3.1 nm with the octadecyl side chains

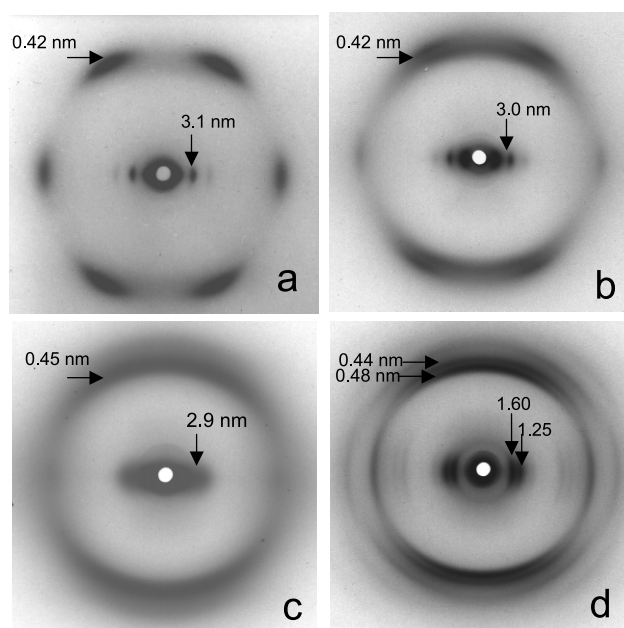


Fig. 4. X-ray diffraction patterns of oriented films of polymers: (a) PAALA-18; (b) *co*PAALA-18,Bn (68:32); (c) *co*PAALA-18,Bn (44:56); (d) PABLA.

crystallized in a hexagonal lattice with a 100 interplanar distance of 0.42 nm. On the other hand, the pattern obtained for PABLA shows discrete off-meridional and equatorial reflections indicative of three-dimensional order compatible with a mixture of hexagonal and tetragonal lattices such as those described for short alkyl-side chain PAALA-*n* [6]. *co* PAALA-18,Bn (68:32) is the only copolymer displaying intense discrete off-meridional spots at 0.42 nm characteristic of phase A. For higher contents in benzyl units, the off-meridional scattering spread and its associate spacing increased up to 0.45 nm indicating that the paraffinic phase was in a disordered state. Moreover, the spacings associated to the equatorial reflections decreased to 2.9 and 2.7 nm for *co* PAALA-18,Bn (44:56) and *co* PAALA-18,Bn (12:88), suggesting that phase B and phase C were the structures present in these two copolymers, respectively, at room temperature.

A stretched film of *co* PAALA-18,Bn (68:32) prepared as indicated above, displayed the sequence of colors shown in Fig. 5 when observed under the cross-polarized microscope. The changes took place instantaneously and were fully reversible. The behavior is similar to that observed for PAALA-18 for copolymers *co* PAALA18,4 (70:30) previously studied by us [8] with differences only affecting to the temperature values at which color switching occurs (Table 3). *co* PAALA-18,Bn (44:56) invariably displayed a blue color similar to that observed for *co* PAALA-18,Bn (68:32) upon heating above 100 °C. Conversely, *co* PAALA-18,Bn (12:88) showed no color but only silvery birefringence. This is the behavior that should be expected for phase B and phase C, respectively, in full agreement with the DSC and X-ray diffraction results described earlier.

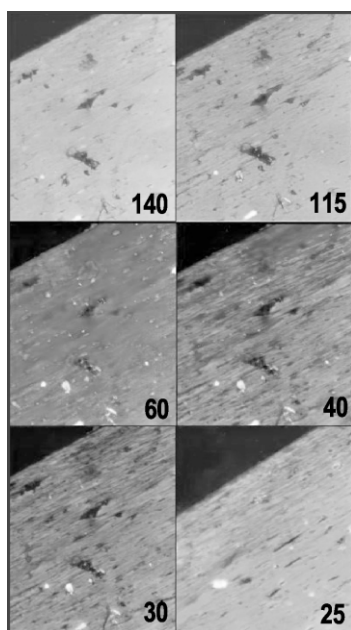


Fig. 5. A series of polarizing optical micrographs from a film of PAALA-18,Bn (68:32) heated at the indicated temperatures (°C).

Table 3

Thermochromic changes in copolymers *co* PAALA-18,Bn

Polymer	$T_{(A \rightarrow B)}$ (°C) ^a	ΔT (°C) (color domains) ^b			
		Orange	Red-violet	Blue	white
PAALA-18 ^c	54–64	25–50	50–65	65–80	170
<i>co</i> PAALA-18,Bn (68:32)	38–50	25–48	48–65	65–140	n.o.
(44:56)	n.o.	n.o.	n.o.	25–140	n.o.
<i>co</i> PAALA-18,4 ^c (70:30)	40–50	25–35	35–44	45–64	65
(50:50)	46–58	25–30	30–40	40–58	58

^a Determined by DSC.

^b Estimated by cross-polarized optical microscopy.

^c Taken from Ref. [8].

4. Conclusions

A series of copoly(β,L-aspartate)s containing long linear alkyl side chains and benzyl side groups have been prepared by anionic ring copolymerization in solution of mixtures of (*S*)-4-octadecoxycarbonyl and (*S*)-4-benzyloxycarbonyl 2-azetidinones. The copolymers have a composition slightly enriched in benzyl units with respect to the composition of the feed and have a random microstructure. They adopt the helical conformation characteristic of poly(β,L-aspartate)s and form laminar arrangements in the solid state with the alkyl side chain crystallized in a separated paraffinic phase when the content in octadecyl groups is majority. In this case, the copolymer shows thermochromic behavior with color changes taking place at temperatures above the melting of the side chain. These results reveal that the benzyl group can be accommodated in the paraffinic phase of the layered structure of comb-like poly(α-alkyl β,L-aspartate)s modifying their thermochromic behavior.

Acknowledgements

This work has been supported by CONICIT (Venezuela), grant No G-97000594, CDCHT-ULA (Venezuela), grant No C-1030-00-08A, and DGICYT (Spain), grant No PB-99-0490. Complementary financial support was received from the Programa de Cooperación Científica con Iberoamérica (MAE, Spain).

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