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Characterization of the Layered Structure in Main Chain Dibenzo-18-crown-6 Ether Polymers by Simultaneous WAXS/MAXS−SAXS/DSC Measurements

Aurora Nogales,* Daniel R. Rueda, Alejandro Sanz, Mari-Cruz García-Gutiérrez, and Tiberio A. Ezquerra

Insituto de Estructura de la Materia, CSIC, Serrano 119, 28006 Madrid, Spain

Mikhail G. Zolotukhin, M. del Carmen G. Hernández, and Sergei Fomine

Instituto de Investigaciones en Materiales, Universidad Nacional Autonoma de Mexico, Apartado Postal 70-360, CU, Coyoacan, 04510, Mexico D. F., Mexico

Howard M. Colquhoun

School of Chemistry, University of Reading, PO Box 224, Whiteknights, U.K.

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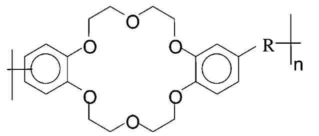
ABSTRACT: The structure and thermal properties of polymers containing dibenzo-18-crown-6 ether units in the main chain linked to an aliphatic spacer of different lengths (C10−C14) is reported. X-ray diffraction patterns of all the studied samples exhibit a peak in the medium angle region, revealing the existence of a lamellar structure. Simultaneous calorimetry and small, medium (SAXS−MAXS) and wide (WAXS) X-ray measurements during cooling and subsequent heating of the samples reveal that a layer phase is formed upon cooling. In the case of the homopolymers, this phase is almost simultaneously accompanied by the appearance of some reflections in the wide angle region as an indication of lateral crystallization. However, by copolymerization, the formation of the layer phase is decoupled from lateral crystallization, being stable in a wide temperature region.

Introduction

Cyclic polyethers (crown ethers) were first discovered by Luttringhaus[1] and later further developed by Pedersen.[2,3] In these early works, it was shown the remarkable ability of crown ethers to be complexed with a great variety of cations. Several macrocycles also became popular starting materials for the building of supramolecular assemblies, sensors for ions, and molecular scaffolds, which thereby stimulated an additional interest within the field. Representative and modern literature on crown ethers can be found in references published elsewhere.[4−6] The incorporation of crown ethers into polymer chains offers additional advantages for their application, such as ease of handling, facility of recovery, and modification of their complexation properties.[7−9] Besides, crown-containing polymers are of major interest as new membrane materials. In addition, due to the disk-like molecular shape of the dibenzo-18-crown-6 ether moiety it seems also foreseeable that mesogenic behavior for these new polymers might be observed. In a previous work, the synthesis and chemical characterization of a new series of film forming polymers containing crown ether groups in their main chain are described.[10] The aim of the present work is to show that linking dibenzo-18-crown-6 ether by aliphatic spacers of variable length, with an even number of carbon atoms in the main chain produces a family of crown ether polymers capable of self-organizing into a nanostructured lamellar arrangement. The structural variations provoked by thermal treatment clearly illustrate the important role of spacer length in controlling the perfection of the lamellar structure found in these materials. The structural study, accomplished by means of simultaneous differential scanning calorimetry and real time X-ray diffraction, revealed that the destabilization of the layers is due to the lateral crystallization of chain segments.

Scheme 1



Where R are: -(CH$_2$)$_{10}$- Sample 1H

-(CH$_2$)$_{14}$- Sample 2H

Experimental Section

The structural study presented concerns, in particular, to two homopolymers containing in the main chain the dibenzo-18-crown-6 ether unit (DB18C6) linked to aliphatic spacers of different length (see Scheme 1) and two copolymers of both systems. Details of the synthesis and chemical characterization of polymers have been reported previously.[10]

According to NMR data,[10] the ratio of isomer units (*syn*- and *anti*-substituted crown ether moieties) is close to 1 and they are randomly distributed along the polymer chain. The molecular weights M_w and M_n, derived from viscosity measurements, are given in Table 1. Solution cast films of about 100 μm thick were prepared from chloroform solutions for all samples. Most of these samples could be easily drawn manually upon heating strips from those films. Fibers were prepared at about 65 °C by manually stretching of the strip. A differential scanning calorimeter (DSC) (Perkin-Elmer DSC-7) was used for thermal characterization of samples. Heating runs at 10 °C/min were accomplished under a constant flow of nitrogen and using a cryogenic bath of liquid nitrogen to enable temperature scanning from −25 °C. The simultaneous DSC

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* Corresponding author. E-mail: emnogales@iem.cfmac.csic.es. Telephone: +34915616800, ext 2406. Fax:+34915645557.

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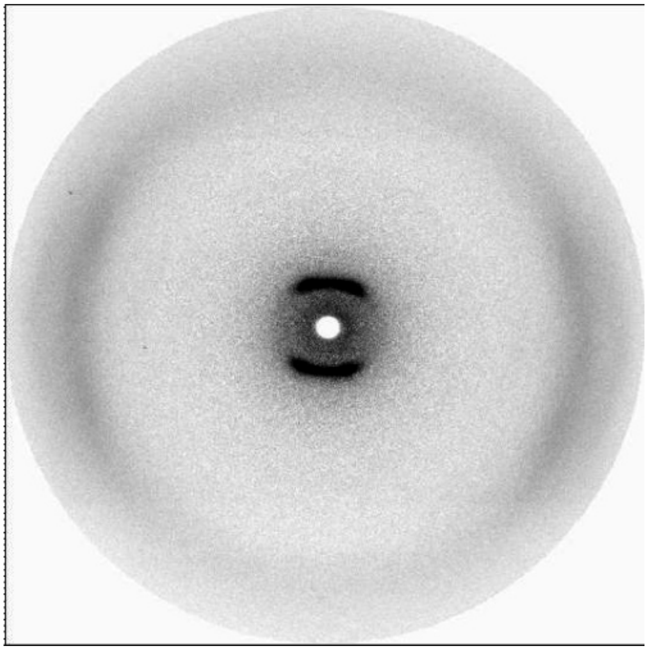

Figure 1. Representative X-ray pattern for a **2H** drawn sample (fiber direction: vertical) showing both the MAXS and WAXS regions investigated here.

Table 1. Molecular Weights (M_w and M_n) for the Samples Studied, Taken from Ref 10, with Spacings for the Medium Angle Reflection, d_1, and Their Apparent Coherence Sizes, D_1, Given for Samples at Room Temperature

polymer code	M_w (g/mol)	M_n (g/mol)	d_1 (nm)	D_1 (nm)
1H	66 070	25 410	2.06	25.0
75/25 1H/2H			2.15	33.3
50/50 1H/2H	57 090	21 010	2.24	39.5
2H	83 800	39 900	2.29	12.1

and X-ray studies of the samples were carried out by using synchrotron radiation on beamline BM26 of the ESRF (Grenoble, France). Simultaneous small−medium- and wide-angle X-ray scattering experiments (SAXS−MAXS and WAXS respectively), during heating of samples at 10 °C/min, were accomplished using a Photonic Science CCD detector and a Multiwire proportional counter detector. A wavelength (λ) of 0.103 nm was used. Accumulation times of 10s were employed. The simultaneous DSC traces were obtained by using a Linkam DSC stage. Pieces of the solution cast film were encapsulated in aluminum pans and melted for 5 min at 180 °C. DSC and X-ray scattering patterns were recorded during cooling at 10 °C/min. Subsequent heating scans were recorded from 30 to 180 °C. For fiber diffraction a 2D MarCCD detector was employed to present in the same image both MAXS and WAXS information. In this case, a sample to detector distance of 22 cm was used.

Results and Discussion

Structure of the Samples at Room Temperature. Figure 1 shows the pattern for a fiber of polymer **2H**. Here some characteristic features of an oriented layered structure are present.[11] In particular, the oriented pattern shows a clear splitting into a four point pattern of the inner reflection (d_1), together with an arc on the meridian, which corresponds to the fiber axis. The angle of the more intense spots with the fiber direction is 22° as measured in the pattern. If one assign the inner reflection to a layer periodicity then the observed splitting can be associated with a tilting of lamellar domains in relation to the fiber direction as is frequently observed in polymers with smectic phases.[11,12] The outer reflection, d_2 around the equatorial direction should be related to molecular distances normal to the chain direction. While d_2 appears in the typical WAXS range, the inner reflection d_1 belongs to the intermediate scattering range known as MAXS.

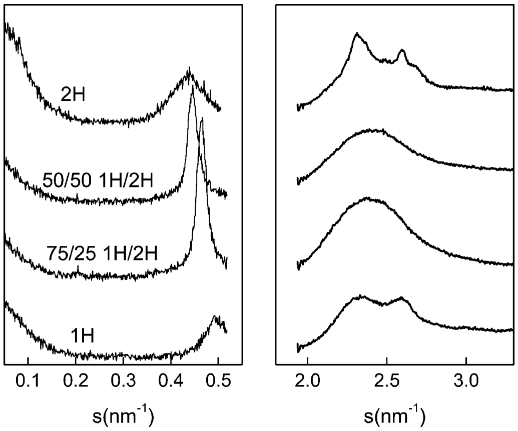

Figure 2. SAXS−MAXS (left) and WAXS (right) diffracted intensity as a function of *s* recorded at room temperature for the two homopolymers (samples **1H** and **2H**) and their copolymers, cooled from the isotropic melt at 10 °C/min.

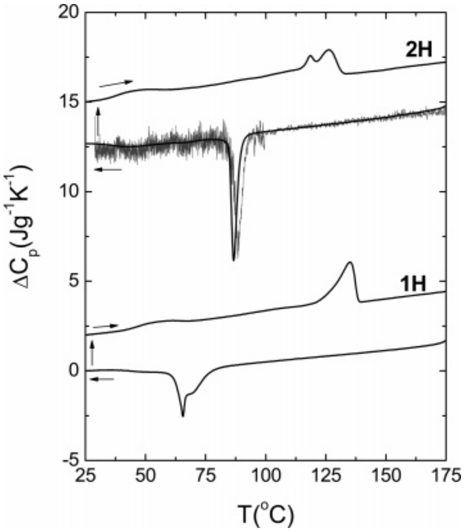

Figure 3. DSC traces of homopolymers **1H2H**, corresponding to cooling from the isotropic melt and subsequent reheating. Superimposed is the DSC trace obtained by simultaneous measuring of calorimetry and wide and medium angle X-ray scattering.

Figure 2 shows the MAXS (left) and WAXS (right) diffracted intensity as a function of the scattering vector *s*, where $s = 2/\lambda(\sin \theta)$ where 2θ is the scattering angle, for the studied samples at room temperature, after being cooled from the isotropic melt at 10 °C/min. In all cases a peak appears in the MAXS region. The spacing values, $d_1 = 1/s_{\max}$, corresponding to the peak of the MAXS patterns, are collected in Table 1. Here, d_1 values are in the range between 2 and 2.3 nm. These spacings are rather similar to those observed for the undrawn solution cast films. The d_1 reflection is quite sharp. An estimation of the “coherent lamellar length” of the reflection d_1 from the reciprocal value of the peak width at half intensity (FWHI) has been obtained. The corresponding values at room temperature are reported in Table 1 as D_1. It is remarkable that the inner reflections, d_1, are much sharper in the copolymers than those observed for homopolymers. The MAXS reflection, d_1, exhibits a clear dependence on the length of the polymer repeating unit and therefore varies with the spacer length. Taking into account the observed size of the DB18C6 molecule (long axis = 1.3 nm and short axis = 0.7 nm)[13] the corresponding

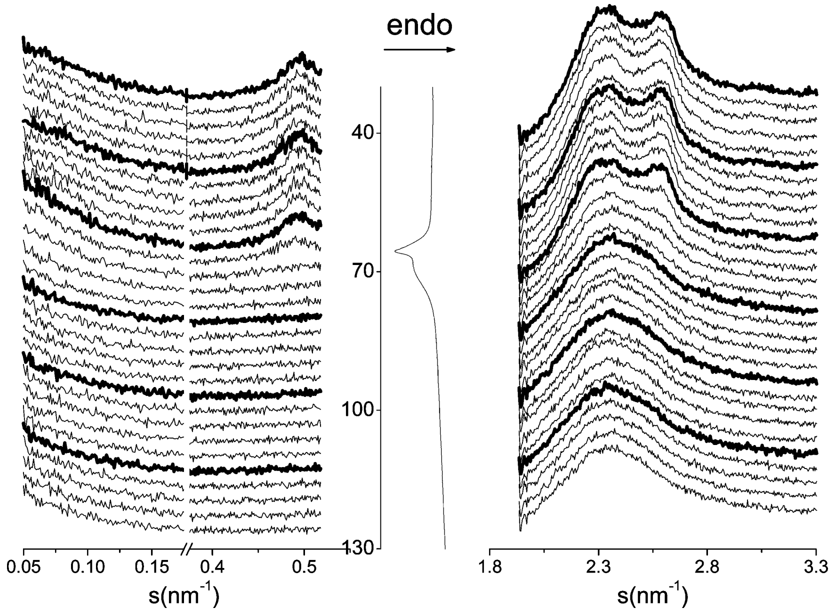

Figure 4. X-ray diffraction patterns in the SAXS−MAXS region (left) and WAXS region (right) of sample **1H** during cooling from the isotropic melt (180 °C) at 10 °C/min down to 30 °C. Only frames from 130 °C to room temperature are presented. In the central panel, the cooling DSC trace is presented for comparison. The vertical axis indicates temperature.

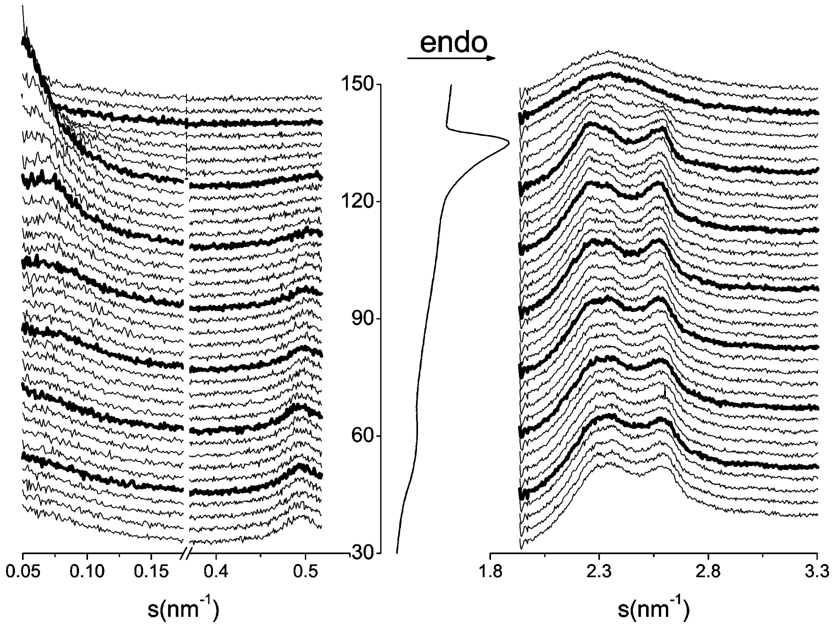

Figure 5. X-ray diffraction patterns in the SAXS−MAXS region (left) and WAXS region (right) of sample **1H** during heating at 10 °C/min. In the central panel, the heating DSC is presented for comparison. The vertical axis indicates temperature.

length of the DB18C6 unit in a polymer chain should be about 1.0 nm, and considering the length of a trans-aliphatic unit (0.127 nm)[14] the calculated length of the repeating unit would be about 2.27 and 2.78 nm for polymers with a spacer of 10 C and 14 C, respectively. Thus, in a first approach, the inner reflection can be associated with the periodicity of a layered structure having a nonextended conformation of the aliphatic spacer. In view of the arclike fiber pattern presented in Figure 1, and considering that the calculated length of the monomer is slightly greater than the d_1 spacing, one may speculate on a tilted arrangement of the chains in the layer structure. The WAXS patterns of the homopolymers **1H** and **2H** exhibit clear Bragg peaks around $s = 2.3$ nm^{-1} and $s = 2.6$ nm^{-1}, and therefore, they are semicrystalline (see Figure 2). However, the 75/25 and the 50/50 **1H**/**2H** copolymers only exhibit an amorphous halo in the WAXS region, centered at 0.41 nm (d_2 reflection). The broadness and shape of the d_2 peak in relation to the sharpness of d_1 would suggest an absence of lateral crystalline order within the lamellar structure in the case of the copolymers. The mean value d_2 (0.41 nm) is compatible with a parallel disposition of crowns.

According to D_1 data (see Table 1 and Figure 2) the layered structure appears better defined for the copolymers relative to the homopolymers. We propose here that this result can be attributed to the absence of lateral crystallization in copolymers when cooled from the melt. As will be shown below, the onset of lateral crystallization is accompanied by a progressive destruction of the layered structure.

Structural Changes During Cooling and Heating. The DSC curves of the homopolymers studied, at 10 °C/min, are shown in Figure 3. Cooling from the melt, an exothermic transition is observed for the two homopolymers. Depending on the length

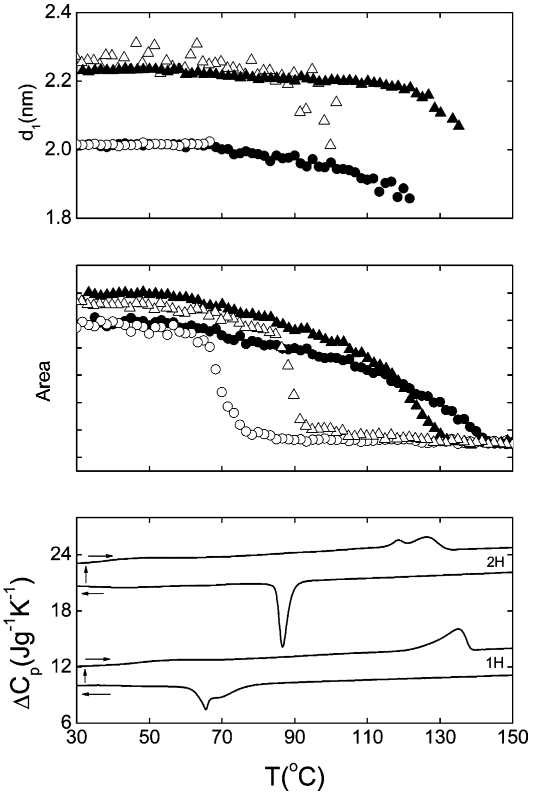

Figure 6. Variation of the MAXS spacing (d_1, top panel) and total area (central panel) during cooling from the isotropic melt (open symbols) and subsequent heating (filled symbols). Circles correspond to values from sample **1H** and triangles for sample **2H**. DSC curves are shown in the bottom panel for comparison.

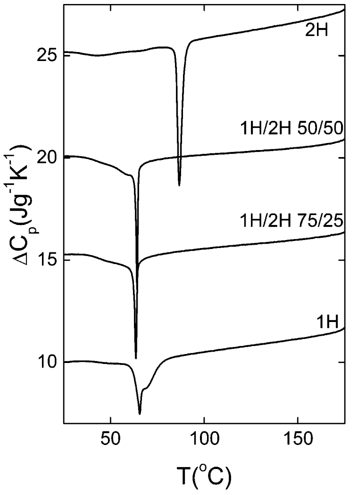

Figure 7. Cooling DSC traces of the homopolymers and two copolymers obtained at 10 °C/min. Labels indicate the molar proportion of each monomer in the copolymer.

of the aliphatic spacer the position and shape of the transition is different, occurring at lower temperature for the shortest spacer. Upon subsequent heating at 10 °C/min, the DSC traces presented in Figure 3 exhibit an endothermic transition, that in the case of the sample with the longer aliphatic spacer (sample **2H**) is clearly a double peak. Around 47 °C, in both homopolymers, a step-like transition, assigned to the glass transition is observed. The wide and medium angle X-ray patterns obtained, simultaneously with the DSC traces, during cooling at 10 °C/min for sample **1H** are presented in Figure 4 and th ose obtained during subsequent heating are shown in Figure 5. The characteristic features of the observed medium angle reflection appearing below 75 °C as a function of temperature are presented in Figure 6.

The SAXS−MAXS and WAXS results obtained during the cooling of homopolymer **1H** and presented in Figure 4 revealed the growth of a reflection around $s = 0.49\ \text{nm}^{-1}$ and an excess of scattering at small angle. Discrete distortions in the amorphous halo occur simultaneously with the appearance of this medium angle reflection. Similar results are obtained for homopolymer **2H**. These results indicate the presence of a layered phase that is accompanied by a process of lateral crystallization upon cooling. When the system is heated again at 10 °C/min, the reflections in the WAXS region become better defined, but at temperatures above 120 °C, melting of the laterally ordered structure begins. Together with the changes observed in WAXS, an intensification of the SAXS excess is observed that evolves to a clear maximum located around $s = 0.08\ \text{nm}^{-1}$ at $T = 100$ °C. In the temperature interval where the WAXS Bragg reflections are disappearing, the SAXS peak becomes more intense and starts to shift toward lower angles, until it eventually disappears. These features are similar to those observed in the melting of many polymeric systems.[15] What it is peculiar for this polymeric system is the presence of a medium angle reflection. Figure 6 shows the evolution of the medium angle spacing (top panel) and its area (bottom panel). Results were obtained during cooling and heating cycles for both homopolymers. As the temperature decreases, the MAXS spacing increases, initially very fast, and it levels off at temperatures at which, in the DSC traces, the exothermic transition is complete. Upon subsequent heating, both homopolymers exhibit a similar behavior. In the lowest temperature range, the spacing remains constant, but in the medium-temperature range, it starts to decrease slowly, and finally it decreases abruptly when the MAXS peak disappears. A similar trend is observed for the area of the MAXS peak.

In an attempt to distinguish the scenario where a pure layered phase is created and subsequent 3D crystallization occurs from that in which all the observed reflections correspond to a crystalline form with poor lateral order we investigated two copolymers of **1H** and **2H**. Specifically we have followed the behavior of the random copolymers with **1H** molar concentrations of 50% and 75%. Figure 7 shows the FSC thermogram of these copolymers during cooling at 10 °C/min compared to those of the homopolymers. As shown in Figure 7, the two copolymers display an exothermic transition upon cooling from the isotropic melt. In both copolymers the transition is located close to the temperature region of the endothermic transition in homopolymer **1H**. However, in contrast to the homopolymer, for the copolymer case the transition is quite sharp. This may be an indication of the formation of the layered structure without any lateral order. To confirm this, we carried out simultaneous WAXS, MAXS, and SAXS on the copolymers during cooling at 10 °C/min. The obtained results for the copolymer 75/25 **1H**/**2H** are presented in Figure 8 and those obtained in the subsequent heating at 10 °C/min are shown in Figure 9. During cooling, a clear peak is developed in the medium angle region without any indication of lateral crystallization in the wide angle. Similar results are obtained for the copolymer 50/50 **1H**/**2H**. From that we may conclude that a pure layered phase is developed in these copolymers. Upon heating, the behavior of the simultaneous SAXS, MAXS and WAXS is very illustrative. At room temperature, the presence of a very sharp and intense MAXS reflection with no SAXS and no Bragg peaks superimposed to the amorphous halo indicates that we are dealing with a purely layered structure. In the temperature interval 58 °C <

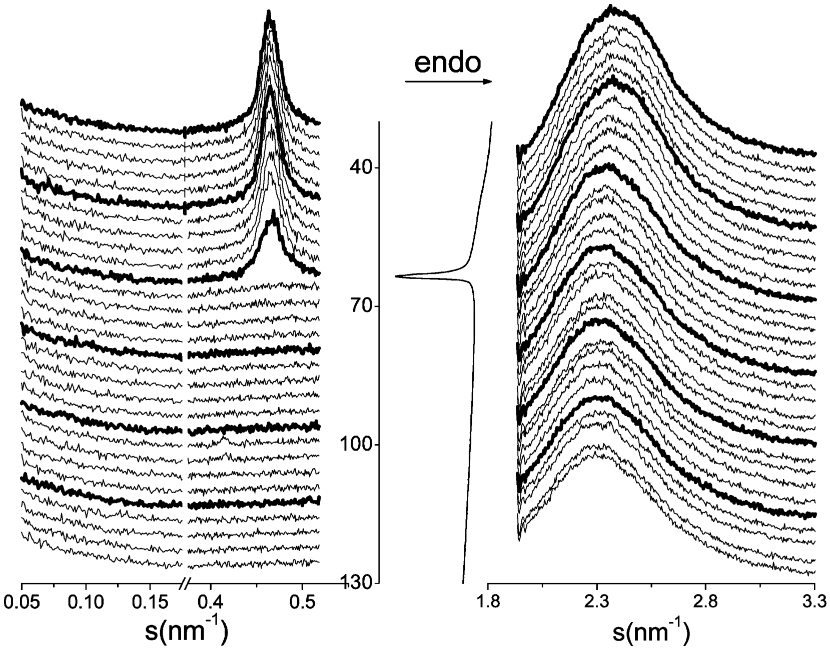

Figure 8. X-ray diffraction patterns in the SAXS−MAXS region (left) and WAXS region (right) of 75/25 copolymer **1H**/**2H** during cooling from the isotropic melt (180 °C) at 10 °C/min to 30 °C. Only frames from 130 °C to room temperature are presented. In the central panel, the cooling DSC is presented for comparison. The vertical axis indicates temperature.

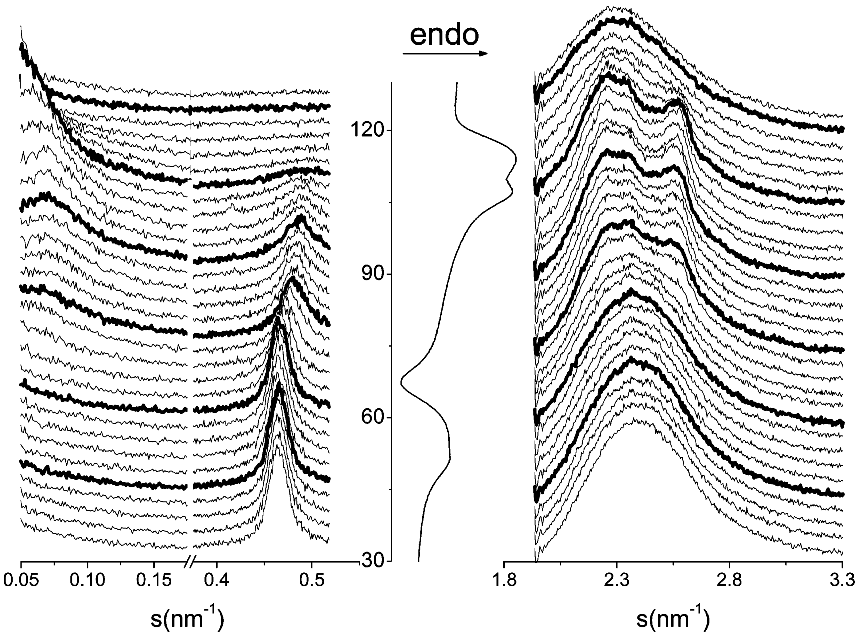

Figure 9. X-ray diffraction patterns in the SAXS−MAXS region (left) and WAXS region (right) of sample **1H**/**2H** 75/25 during heating at 10 °C/min. In the central panel, the cooling DSC trace is presented for comparison. The vertical axis indicates temperature.

$T < 82$ °C, the intensity of the MAXS reflection starts to decrease and it becomes broader and it shifts toward higher angles (lower spacings). In this temperature range, an excess of SAXS is observed, and the WAXS halo starts to exhibit the Bragg reflections superimposed to the amorphous halo. At temperatures above 82 °C the SAXS has clearly evolved to a peak located around $s = 0.07$ nm^{-1}. This observation reveals that the simultaneous development of SAXS intensity with the Bragg peaks in the WAXS region is related to lateral crystallization. Finally, at higher temperatures, the laterally ordered structure starts to melt and all the reflection in the scattering patterns disappear except for the amorphous halo. The characteristics of the developed medium angle reflection in the copolymers, as a function of the temperature, are presented in Figure 10. The DSC traces are also presented for comparison. The double endothermic peak observed in the heating DSC traces for the 75/25 copolymer **1H**/**2H** resembles that observed for sample **2H** (Figure 3). Taking into account the variation of the spacing d_1 (Figures 6 and 10) upon heating the samples, it seems that the layered structure is more stable in the case of the sample based on long aliphatic spacers. Thus, while d_1 for **1H** decreases continuously about the softening point, sample **2H** and the copolymers present a second temperature range where d_1 slightly decreases previous to the melting of the material. This could be the origin of the double melting peak in the samples with long aliphatic spacers.

From the obtained results, one may conclude that, in the case of the copolymers, a pure layered structure appears on cooling. Upon heating, lateral crystallization is favored. However, this

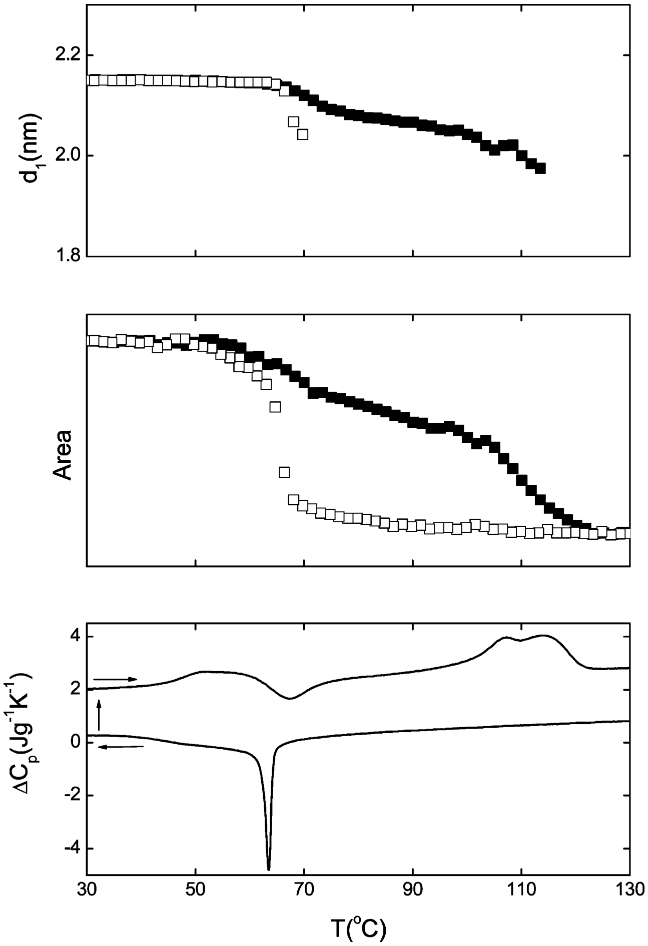

Figure 10. Variation of the MAXS peak spacing (d_1, top panel) and total area below the MAXS reflection (central panel) during cooling from the isotropic melt (open symbols) and subsequent heating (filled symbols) for 75/25 copolymer **1H**/**2H**. DSCs curves are shown in the bottom panel for comparison.

lateral crystallization implies a destruction of the initial layered structure, as indicated by the broadening of the MAXS reflection; i.e., there is a loss in apparent coherence size D_1, with the development of lateral crystallization.

Conclusions

The results presented here show that polymeric materials based on the dibenzo-18-crown-6 ether unit linked to aliphatic spacers form layered structures. When the regularity of the chain is high, the formation of the layered phase is nearly simultaneous with a lateral crystallization process, inhibiting a pure layered structure. Stabilization of this layer phase at temperatures above the glass transition can be achieved by copolymerization of monomers containing different spacer lengths.

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