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Main-Chain Chiral Poly(2-oxazoline)s: Influence of Alkyl Side-Chain on Secondary Structure Formation in the Solid State

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Summary: The influence of the side-chains of main-chain chiral poly(2-oxazoline)s on their thermal properties was investigated using differential scanning calorimetry (DSC) and the nature of the obtained melting endotherms was further investigated by thermal annealing of the polymers. Poly(R-2-ethyl-4-ethyl-2-oxazoline) (p-R-EtEtOx) was found to be amorphous, while polymers with longer side-chains are semi-crystalline. Previously we reported that the chirally ordered crystals of poly(R-2-butyl-4-ethyl-2-oxazoline) (p-R-BuEtOx) have a high melting temperature of more than 200 °C. In this work we demonstrate that elongation of the side-chains from butyl to octyl results in a decrease in the crystallization rate and melting temperature suggesting that the chirally ordered crystals of p-R-BuEtOx are based on close packing of the main-chain enhancing dipolar interactions between the tertiary amide moieties. Crystallization of chiral polymers with longer side-chains results may then be driven by close packing of the side-chains. This is supported by the observation that further elongation of the side-chain length increases the crystallization rate. Moreover, an additional melting endotherm appears for these polymers at a lower temperature upon annealing ascribed to a dual crystal size population. Circular dichroism (CD) measurements of the semi-crystalline main-chain chiral polymer films revealed the presence of chirally ordered crystals while X-ray diffraction (XRD) patterns revealed a closer packing of the chiral poly(2-alkyl-2-oxazoline)s compared to the non-chiral polymers, suggested to result from the chiral ordering in the crystals. Grazing incidence wide angle x-ray scattering (GIWAXS) patterns indicated that the chiral crystals of p-R-BuEtOx do not form a helical structure, however, the substrate does influence the type of structure formed.

Keywords: chiral polymers; circular dichroism; grazing incidence wide angle X-ray scattering (GIWAXS)

Introduction

In nature most polymers are chiral, like proteins and DNA. The chirality of these

polymers together with the presence of non-covalent interactions, such as hydrogen bonds, electrostatic interactions and van der Waals interactions controls the

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formation of secondary structures like helices or β -sheets. In contrast to natural polymers only a few examples of synthetic polymers with a secondary conformation stabilized by hydrogen bonds are known.^[1,2] The majority of synthetic polymers that adopt a secondary structure are stabilized by van der Waals interactions. The main-chain of these polymers are often rigid or semi-flexible, which also contributes to the stability of their secondary structure. Since side-chains can significantly influence the rigidity of the backbone, side-chains also affect the potential formation of a secondary conformation. For example, polysilanes can adopt collapsed coil, flexible coil, stiff, or rigid-rod-like conformations depending on the alkyl side-chain length.^[3] Nilsson *et al.* hypothesized that the degree of planarity in the polymer backbone depends on electrostatic, H-bonding, steric, or van der Waals interactions within or between polymer chains, which again controls secondary structure formation.^[4] The effect of the side-chains on the chiral structure of poly(propionic esters) with long alkyl side-chains was illustrated by a helix-sense inversion driven by the change in temperature or solvent composition.^[5] Furthermore, the side-chain can influence the thermal properties. For comb polymers it is observed that side-chain melting can occur with a minimum of eight carbon atoms in the pendant group when the backbone is semi-flexible and with a minimum of twelve carbon atoms when the main-chain is rigid.^[6]

Main-chain chiral poly(2-oxazolines)^[7–11] can be regarded as pseudo-peptides,^[12,13] and, form chirally ordered structures that are stabilized by dipolar

interactions between the tertiary amides, as described in recently published papers.^[14–16] It is hypothesized that varying the alkyl side-chain length could make the backbone more rigid or more flexible and, therefore, could stabilize or destabilize the formation of the chiral secondary structure. The crystallinity can also be influenced by the side-chains, which can affect the optical properties in the solid state.

In this contribution the formation of chirally ordered (semi-crystalline) bulk structures is studied by differential scanning calorimetry (DSC) and circular dichroism (CD) of a small library of main-chain chiral poly(2-oxazolines). Furthermore, the influence of the side-chain as well as the influence of the presence of a chiral group on the crystalline structure was investigated by XRD in drop casted films as well as in the bulk (powder diffraction) and the type of structure formed by poly(R-2-butyl-4-ethyl-2-oxazoline) (p-R-BuEtOx) in spin-coated films was determined by grazing incident wide-angle X-ray scattering (GIWAXS) measurements (Scheme 1).

Experimental Part

The syntheses of the investigated polymers are described in previously published papers.^[14–16]

Thermal transitions were determined on a DSC 204 F1 Phoenix by Netsch under a nitrogen atmosphere with cooling and heating rates of 10 or 20 °C/min.

CD spectra were measured on a Jasco J815 spectropolarimeter equipped with a Linkam temperature controller for temperatures ranging from 20 to 250 °C. The

Scheme 1.

Schematic overview of the investigated polymers.

samples were spin coated from chloroform (20 mg/mL) on a quartz slide for 2 minutes with 2000 rpm. The following scanning conditions were used: 50 nm/min scanning rate; 1 nm bandwidth; 0.1 nm datapitch; 0.5 s response time; and 10 accumulations.

XRD patterns were recorded with a Rigaku Model RU200 X-ray apparatus equipped with a rotating anode generator. Diffraction angles are for Cu K α radiation. A stepscan was performed on each sample with 0.02 datapitch and 1.5 s response time. Poly(2-alkyl-2-oxazoline)s and chiral poly(2-alkyl-4-ethyl-2-oxazoline)s were drop casted from concentrated chloroform solutions onto glass substrate. The polymer films were heated to above melt temperature and slowly cooled to room temperature. The chiral poly(2-alkyl-4-ethyl-2-oxazoline)s were annealed in an oven to induce crystallization. The poly(2-alkyl-2-oxazoline)s were directly measured after the sample preparation except for poly(2-methyl-2-oxazoline), which has been stored for over a year. Powder XRD-spectra of the as synthesized p-*R*-BuEtOx were also taken to determine the bulk structure. The glass substrate attached to the metal sample holder with double sticky tape did not give any signal. No internal standard was used. Additionally, a stepscan powder XRD of p-*R*-BuEtOx with silica as an internal standard has been measured with 0.02 datapitch and 5 s response time to model the type of structure that has been formed.

We performed GIWAXS experiments at the BW4 beam line, at HASYLAB at DESY in Hamburg, Germany. Experiments were carried out in pseudo-grazing incidence configuration at a wavelength of $\lambda = 0.138$ nm, a band width of 10^{-4} and a spot size of $78 \mu\text{m} \times 46 \mu\text{m}$ in horizontal and vertical direction, respectively. The incident polar angle has been set to $\alpha_1 = 0.10^\circ$. Two-dimensional detector patterns were collected with exposure times of 900 s on a CCD-detector (MAR165CCD, pixel size $79.1 \mu\text{m}$). The detector to sample distance was determined by means of a silver behenate standard. Data are cor-

rected for background scattering from the silicon and glass substrate and are presented in (q, Φ) -presentation. Here, $q = 2\pi/d$ is the overall momentum transfer which can be directly related to the distance d of the corresponding scattering planes. Φ denotes the angle between the direction parallel ($\Phi = 0^\circ$) and perpendicular ($\Phi = 90^\circ$) to the sample surface. For more details on the experimental setup and data conversion see reference^[17]. p-*R*-BuEtOx was spincoated from chloroform solution (solution of 5, 10 and 20 mg/mL) on cleaned silica wafers and glass substrates (cleaned with isopropyl alcohol and dried with an air gun) and annealed at 124°C for at least 1 hour to induce crystallization.

Results and Discussion

Recently, we reported the thermal properties of p-*R*-BuEtOx, whereby it was found that this polymer exhibits a glass transition temperature ($T_g = 52^\circ\text{C}$) followed by cold crystallization ($T_{cc} = 160^\circ\text{C}$) and a double melting peak ($T_{m1} = 197^\circ\text{C}$ and $T_{m2} = 221^\circ\text{C}$) upon heating at $20^\circ\text{C}/\text{min}$ due to melt-recrystallization.^[15] Since the racemic polymer was found to be completely amorphous, at least within the DSC sensitivity, the crystallinity was ascribed to be the result of its chirality, allowing regular packing of the polymer chains. To investigate the effect of the side-chain length on the thermal properties of such main-chain chiral poly(2-oxazoline)s, the thermal properties of other chiral poly(2-alkyl-4-ethyl-2-oxazoline)s were analysed by differential scanning calorimetry (DSC) and will be discussed in the following. The synthesis of these main-chain chiral polymers with a chiral ethyl substituent in the main chain was performed by living cationic ring-opening polymerization as we have recently reported.^[16]

At first, the effect of decreasing the side-chain length of the chiral polymers from a butyl- to an ethyl-group was investigated. This p-*R*-EtEtOx polymer only revealed a T_g at 92°C with a heat capacity (ΔC_p) of

Figure 1.

DSC traces of p-R-EtEtOx of the second heating run and after annealing at 120 °C for 24 h (heating rate = 20 °C/min).

0.38 J/g·K by DSC (Figure 1). No melting endotherm (T_m) was found up to a temperature of 250 °C even not after annealing above the T_g at 120 °C for 24 hours. This results indicate that this polymer is completely amorphous like poly-2-ethyl-2-oxazoline (pEtOx), although it should be noted that the sensitivity of DSC is limited and if there would be a very minor fraction of a crystalline phase this would not show up in the measurements.^[18] Nonetheless, these results demonstrate that the ethyl side-chains are on the one hand too short to crystallize while on the other hand they apparently hamper packing of the main chain.

In a next step the side-chain length of the main-chain chiral poly(2-oxazoline) was increased from a butyl- to an octyl-group in p-R-OctEtOx. The second heating run in DSC also showed no melting endotherm (not shown). Since a melting peak appeared in the first heating run (not shown), we tried long annealing times (t_a) at 60 °C to induce crystallization. The polymer needed to be annealed for at least 12 hours at 60 °C to obtain a small detectable amount of crystals with a T_m of 112 °C (Figure 2a). The crystalline fraction increased with increasing annealing time and leveled off after 30 hours (Table 1). An annealing temperature (T_a) between 60

Figure 2.

DSC traces of p-R-OctEtOx (a) after annealing at 60 °C for different annealing times (10 °C/min) and (b) after annealing for 33 h at different annealing temperatures (20 °C/min).

Table 1.Thermal properties of p-R-OctEtOx after annealing ($T_a = 60^\circ\text{C}$: $10^\circ\text{C}/\text{min}$ and $t_a = 33\text{ h}$: $20^\circ\text{C}/\text{min}$).

t_a (h)	$T_a = 60^\circ\text{C}$		$t_a = 33\text{ h}$		
	T_m ($^\circ\text{C}$)	ΔH (J/g)	T_a ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	ΔH (J/g)
12	112	0.3	30	–	–
15	112	0.5	40	–	–
18	112	2	50	114	6
21	113	4	60	115	19
24	113	7	70	119	20
27	113	11	80	122	13
30	113	14	90	126	1
33	113	15	100	–	–

and 70°C resulted in the highest fraction of crystals after 33 hours and T_m was found to increase from 115 to 122°C when the T_a is increased from 60 to 80°C , indicating the formation of more perfect crystals at higher T_a (Table 1 and Figure 2b). Compared to p-R-BuEtOx the T_m of p-R-OctEtOx is much lower and long annealing times are necessary in order to form crystals. Therefore, it may be speculated that the crystallinity of p-R-OctEtOx is due to side-chain crystallization. Moreover, the melting endotherm is close to the melting temperature of non-chiral semi-crystalline poly(2-alkyl-2-oxazoline)s, which have a T_m of $\sim 150^\circ\text{C}$.^[18] It is proposed that the more rigid and bulky chiral main-chain hinders crystallization of the octyl side-chains, making long annealing times necessary. Moreover, the presence of the ethyl main-chain substituent and the chiral organization results in less stable crystals

leading to a lower T_m . It might be speculated that besides side-chain crystallization also main-chain crystallization, i.e. amide dipolar interactions, occurs in p-R-BuEtOx. Due to the smaller side-chain interaction between the amide-moieties are possible, which could explain the much higher T_m of p-R-BuEtOx ($T_m = 210^\circ\text{C}$) compared to p-R-OctEtOx.

Subsequently, the side chain length was further extended to nonyl and undecyl chains resulting in p-R-NonEtOx and p-R-UndeEtOx, which showed comparable behavior (Figures 3 and 4). Both polymers revealed a double melting peak in the first heating run. However, p-R-NonEtOx did not show a melting transition in the second heating run (not shown) while p-R-UndeEtOx shows cold crystallization ($T_{cc} = 40^\circ\text{C}$, $\Delta H_{cc} = -39\text{ J/g}$) in the second heating run (Figure 4a). From these results it can be concluded that the crystallization rate of

Figure 3.

DSC traces of p-R-NonEtOx (a) after annealing for 2 h at different annealing temperatures ($20^\circ\text{C}/\text{min}$) and (b) after annealing at 40°C for different annealing times ($20^\circ\text{C}/\text{min}$).

Figure 4.

DSC traces of p-R-UndeEtOx (a) of the second heating run (10 °C/min), (b) after annealing for 1 hour at different annealing temperatures (20 °C/min), (c) after annealing at 40 °C for different annealing times (20 °C/min).

the main-chain chiral poly(2-oxazoline) *s* increases when the side-chain length is increased from octyl side-chains to nonyl and undecyl side-chains, indicating that these polymers indeed undergo side-chain crystallization. This can be ascribed to the parts of the side-chain further away from the backbone that have more flexibility to adopt ideal packing conformation favoring crystallization. Upon annealing of p-R-NonEtOx for 2 hours at 20 °C a double melting endotherm in the temperature

range between 85 and 105 °C was observed. The double melting endotherm is due to melt-recrystallization since ΔH_{m2} decreases and ΔH_{m1} increases and T_{m1} moves to higher temperature with increasing T_a (Table 2; Figure 3a). In contrast to the first heating run, no melting endotherm in the temperature range between 60 and 85 °C is observed. However, when the annealing time is increased, also a double melting endotherm (T_{m3} and T_{m4}) is visible in this temperature range (Table 2;

Table 2.

Thermal properties of p-R-NonEtOx after annealing (20 °C/min).

$t_a = 2 \text{ hours}$				$T_a = 40 \text{ °C}$						
T_a (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)	t_a (h)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)	T_{m3} (°C)	T_{m4} (°C)	ΔH_m (J/g)
20	88	102	0.4	1	–	–	–	–	–	–
30	90	100	0.4	2	92	101	0.4	–	–	–
40	91	102	0.7	3	91	102	1	–	70	0.2
50	94	103	0.8	4	91	101	3	66	71	0.4
60	97	–	0.8	5	91	101	8	66	70	0.8
70	–	–	–	6	90	101	7	65	70	3

Table 3.

Thermal properties of p-R-UndeEtOx after annealing (20 °C/min).

$t_a = 1 \text{ hour}$				$T_a = 40 \text{ }^{\circ}\text{C}$				
$T_a \text{ (}^{\circ}\text{C)}$	$T_{m1} \text{ (}^{\circ}\text{C)}$	$T_{m2} \text{ (}^{\circ}\text{C)}$	$\Delta H_m \text{ (J/g)}$	$t_a \text{ (h)}$	$T_{m1} \text{ (}^{\circ}\text{C)}$	$T_{m2} \text{ (}^{\circ}\text{C)}$	$T_{m3} \text{ (}^{\circ}\text{C)}$	$\Delta H_m \text{ (J/g)}$
30	93	103	2	1	94	105	–	3
40	94	104	4	2	94	105	–	28
50	97	105	4	3	93	105	73	47
60	99	–	3	4	93	105	74	57
70	–	–	–	5	93	105	74	59
80	–	–	–	6	93	105	75	59

Figure 3b). Similarly, annealing the polymer for 1 hour at 30 °C resulted in a double melting endotherm between 85 and 110 °C due to melt-recrystallization (Table 3; Figure 4b). By increasing the annealing time, a third melting endotherm (T_{m3}) appeared in the temperature range between 60 and 80 °C (Table 3; Figure 4c). The melting peaks (T_{m1} and T_{m2}) at the higher temperature appeared after shorter annealing times than the melting peak (T_{m3}) at lower temperature. This indicates that the melting peaks are possibly caused by a dual crystal size population where the melting temperature is lower for the smaller sized crystals.^[19] Another explanation could be the presence of a second chirally ordered structure.

The formation of chiral secondary structures should be further investigated by CD measurements on spin-coated polymer films. p-R-BuEtOx crystallizes upon heating around 100 °C and also the Cotton effect at 198 nm increased signifi-

cantly in size at this temperature, indicating that the p-R-BuEtOx crystals that are formed are chirally ordered, as discussed in our previous work.^[15]

p-R-EtEtOx is an amorphous polymer and a spin-coated one revealed a weak dichroic Cotton effect at all temperatures (Figure 5a). The Cotton effect caused by the n- π^* transition decreases in strength with increasing temperature. These observations indicate that some chiral order is present in the amorphous polymer, which decreases with increasing temperature. The spin-coated p-R-OctEtOx film revealed very similar behaviour indicating that this polymer does not crystallize in the thin film (Figure 5b).

The spin-coated p-R-NonEtOx and p-R-UndeEtOx films also revealed a weak dichroic Cotton effect, just like p-R-EtEtOx and p-R-OctEtOx (Figure 6). However, at 50 °C the Cotton effect inverts in sign and becomes stronger. These results indicate that crystals start to form during

Figure 5.

Temperature dependent CD spectra of a p-R-EtEtOx and p-R-OctEtOx spin-coated films.

Figure 6.

Temperature dependent CD spectra of p-R-NonEtOx (a and b) and p-R-UndeEtOx (c and d) spincoated films.

the measurements at 50 °C, which apparently causes an inversion in sign due to a different organization of the chiral units. At 80 °C the highest CD signal is obtained indicative of the highest crystalline fraction and further heating leads to melting of the crystals until an amorphous film is obtained again at 130 °C, which causes the reverse in sign of the Cotton effect.

In general, crystallization has mainly an effect on the Cotton effect caused by the $n\text{-}\pi^*$ transition for p-R-NonEtOx and p-R-UndeEtOx, while the Cotton effect caused by the $\pi\text{-}\pi^*$ transition is mainly increased in strength when p-R-BuEtOx crystallizes. This difference might be interpreted as a difference in crystallinity; the crystals of p-R-BuEtOx are proposed to be stabilized by a combination of side-chain and main-chain crystallization (dipolar interactions), while longer side-chains lead to stronger side-chain interactions apparently obstructing close packing of the

main-chains. This proposed difference in crystallization mechanisms could also explain the large observed differences in the melting temperatures.

The type of structures formed was further investigated by XRD. To investigate the influence of the chiral main-chain substituent, non-chiral poly(2-alkyl-2-oxazoline)s were also measured. Fibre drawn structures of poly(2-oxazoline)s measured by Litt *et al* indicated that the most probable structure is a planar, twisted configuration with the lateral groups tilted and fully extended, alternating on each side of the main chain.^[20] All poly(2-alkyl-2-oxazoline)s investigated here reveal peaks at 2θ equal to 13.9° (#4) and 16.9° (#5), corresponding to a d-spacing of 0.63 and 0.52 nm, respectively, together with a small peak at 18.5° (0.48 nm #6) (Figure 7, Table 4). These peaks are also observed for the amorphous poly(2-methyl-2-oxazoline) (pMeOx) and poly(2-ethyl-2-

Figure 7.

XRD spectra of drop casted poly(2-alkyl-2-oxazoline)s.

oxazoline) (pEtOx). The side-chains of these polymers are too short to crystallize and therefore these peaks originate from backbone ordering. Litt et al. determined the periodicity of a fibre drawn poly(2-oxazoline)s to be 0.64 nm, which indicated that the backbone was not fully extended.^[20] We observed the same for the drop casted polymers investigated here. The semi-crystalline polymers with propyl side-chains or longer reveal an additional peak (#1) located at lower angles which corresponds to the long-spacing. In agreement with the results of Litt et al. the long-spacing increases linearly with increasing side-chain length.^[20] The authors concluded that the side-chains must be tilted about 36° from the direction perpendicular to the chain axis. In agreement to the results of Cai and Litt the poly(2-nonyl-2-oxazoline) (pNonOx) revealed two additional peaks (#2 and #3).^[21] The values in

Table 4 do not fit exactly to the values found by Litt et al. which is probably the result of a different sample preparation, i.e. Litt et al. measured aligned fibers while we measured drop casted films without the use of an internal standard. The peaks observed at higher scattering angles (#5 to #8) corresponding to spaces of 0.52, 0.48, 0.43 and 0.35 nm, are comparable to those detected by Schlaad et al.^[22] for poly(2-isopropyl-2-oxazoline) (PIPOX) crystallized above its lower critical solution temperature (LCST) and PIPOX nanofiber coagulates (0.543, 0.485, 0.413 and 0.37 nm).

For the main-chain chiral polymers in which the 4-position is substituted with an ethyl group, the long spacing decreases, i.e. the polymers crystallize in a closer packed structure compared to their non-chiral polymers (Figure 8, Table 5). The scattering peaks (#4 to #8) corresponding to

Table 4.

d-Spacings of drop casted poly(2-alkyl-2-oxazoline)s.

Polymer / d-spacing (nm)	Long-spacing	2	3	4	5	6	7	8
pMeOx	–	–	–	0.63	0.52	0.48	–	–
pEtOx	–	–	–	0.63	0.53	0.48	–	0.35
pPropOx	1.17	–	–	0.63	0.52	0.48	0.43	0.35
pBuOx	1.38	–	–	0.63	0.52	0.48	0.43	0.35
pNonOx	2.26	1.16	0.78	0.63	0.52	0.48	0.43	–

Figure 8.

XRD pattern of drop casted chiral poly(2-alkyl-4-ethyl-2-oxazoline)s.

spacings of 0.63, 0.52, 0.48 and 0.35 nm were also found for the non-chiral poly(2-oxazoline)s. The peak intensities depend on the annealing times. The XRD spectrum of p-R-UndeEtOx shows compared to the spectra obtained for p-R-OctEtOx and p-R-BuEtOx much weaker peaks. The XRD pattern of p-R-NonEtOx was left out since only very weak peaks were detected. All chiral polymers show a peak or shoulder at 1.73 nm, which may be a spacing induced by the ethyl substituents present on the polymer main chains.

The type of structure that is formed in a p-R-BuEtOx film was further investigated with GIWAXS measurements. The polymer was spincoated from chloroform solutions with three different concentrations onto glass and silica substrates. After spin coating, the polymer films were annealed at 140 °C to induce crystallization. With the increasing film thickness, a more random orientation of the domains relative to the substrate is

observed (isotropic scattering). This could also explain the different CD spectra of p-R-NonEtOx spincoated from different concentrations. Besides the film thickness, also the type of substrate influences the type of ordering. Figure 9 compares the representative two-dimensional detector pattern obtained for p-R-BuEtOx films deposited from a 10 mg/mL solution onto silicon and glass substrates, respectively. Based on the GIWAXS results it seems that p-R-BuEtOx does not form a helical structure. The unit cell is rhomboedric. Silicon seems to planarize the conformation resulting in a planar, mirror inverted stacking of the backbones. This is similar to poly(ethylene imine) hydrates which are also planar zigzag.^[23] Extinction rules lead to the absence of the odd reflections of the stacked layers. This is different on glass. The symmetry group seems to be different and therefore a strong first order reflection is visible which may be due to a twist along the backbone. The small

Table 5.

d-Spacings of drop casted chiral poly(2-alkyl-4-ethyl-2-oxazoline)s.

Polymer	d-spacing (nm)	Long-spacing*	2*	3	4	5	6	7	8
p-R-BuEtOx	1.73	0.95	0.78	–	0.63	0.52	0.48	0.43	0.35
p-R-OctEtOx	sh	1.40	0.83	0.69	0.63	sh	0.48	0.43	0.35
p-R-UndeEtOx	sh	1.79	0.91	0.76	0.63	0.52	sh	0.43	–

* Assigned as such to have a linear dependence. sh = shoulder

Figure 9.

Two-dimensional detector pattern obtained for p-R-BuEtOx films deposited from a 10 mg/mL solution onto a silicon (left) and glass substrate (right), respectively.

angular spread of the first order reflection suggests that this structure is located close to the substrate surface whereas the pronounced isotropic contribution to the second order peak indicates a more random orientation relative to the substrate of the domains with unperturbed structure in the rest of the film.

Conclusion

From the thermal results obtained for the chiral poly(2-oxazoline)s we conclude that the alkyl side-chains require a certain length before side-chain crystallization can occur: p-R-EtEtOx is completely amorphous while P-R-BuEtOx has a relatively high melting temperature, probably due to a combination of main chain and side-chain crystallization. By increasing the side-chain length from butyl to octyl, a significant drop in the melting temperature is observed, which corresponds to side-chain crystallization, and the crystallization rate of the side-chain crystallization is decreased due to the more bulky, chiral backbone. Further increasing the side-chain length results in an increase in crystallization rate and the presence of a dual lamellae population.

The presence of the chiral main chain substituent leads to a closer packing of the polymer chains compared to the analogues polymers without a substituent on the main chain, based on the decreased long-spacing. It should be noted here that at this point we may speculate that the chiral crystal packing is responsible for the closer packing as most probable explanation. However, future work should include comparison of the racemic and chiral polymers with long side-chains to see how the chirality of the main chain substituent influences the crystal packing of the side-chain crystallization. Furthermore, the GIWAXS results indicated that the chiral p-R-BuEtOx does not form a helical secondary structure, but a planar structure on silica, although a twist might be present when the polymer is spin coated on glass substrate.

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