UCRL-CONF-232815

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Thermally Induced Reorganization in LCP Fibers: Molecular Origin of Mechanical Strength

C. K. Saw, G. Collins, J. Menczel, M. Jaffe

July 18, 2007

2007 NATAS Conference
East Lansing, MI, United States
August 26, 2007 through August 29, 2007

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Updated October 14, 2003

Thermally Induced Reorganization in LCP Fibers: Molecular Origin of Mechanical Strength[#]

Cheng K. Saw*, George Collins[+], Joe Menczel** and Mike Jaffe[+]
*Lawrence Livermore National Laboratory, Livermore, CA 94551
[+] New Jersey Institute of Technology, Newark, NJ 07102
** Alcon Laboratories, Inc, Fort Worth, TX 76134

ABSTRACT

The ordering of liquid crystalline polymer fiber during heat treatment is of great interest for many commercial reasons. This is because, by convention, fiber property can be greatly improved by heat-treatment at below the melting temperature and often such processing conditions are also very complex. There are many variations of such treatments, in terms of temperature, exposure time and whether the fibers are under tension or not. The state-of-the-art technology will be to optimize the desired property without significantly enhancing the undesired properties. The types of heat treatment are highly correlated to the understanding of the mechanism of improving the properties at the molecular level and the microstructures. Using WAXS and synchrotron SAXS techniques, the structure and morphology of our commercial LCP (liquid crystalline polymer), a co-polymer of CO (Vectran[@]) and its variant polymer fiber COTHBP are being examined. Both fibers have the typical liquid crystalline polymer structure, ie, highly ordered across the fiber axis and aperiodic sequencing along the fiber axis. Physical testing has revealed a three fold increase in strength in both fibers, however, the modulus is observed to increase significantly in COTBP and not so much CO. This paper reports on the changes and the differences on the structural and morphological behavior for both the as-spun and heat-treated LCP fibers. We have also use thermal analysis technique to provide a guide to the heat-treatment cycle. We propose an "organized kinks" model to describe the differences between the two polymer fibers. Future publication will focus on the in-situ behavior at elevated temperatures and under heat-treatment.

Portion of this work was performed when the authors were at Hoechst-Celanese. Recent work by CKS was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48

INTRODUCTION

Liquid crystal polymers are of great commercial interest because of many unique properties. By having the polymer chains align such as in the case of fibers, LCP exhibits improved properties over the conventional polymeric materials, like PET (polyethylene teraphalate), PE (polyethylene) and etc, for example, tenacity, modulus, low elongation under stress, high melting point, chemical stability as well as retention of tensile property when exposed to thermal excitation. Our LCP's, for example Vectran@ and its variants are also of great interest because they can be manufactured from melt which is economically desirable, hence it is known as a thermotropic LCP.

Liquid crystalline polymers (LCP) are typically wholly aromatic polyester and polyamide. The chains are somewhat stiff with some level of conformational flexibility. Hence, these chains can readily organize and align themselves under any small fields (e.g. flow, electric or magnetic). Unlike conventional PET (polyethylene terephthalate) fibers, these polymers do not fold. When made into fibers, the molecules align themselves along the direction of the flow, forming highly oriented structures. In theory, such fiber can achieve very high tensile strength as well as modulus. It is known that the necessary conditions to achieve high modulus fibers are high molecular orientation, high ordered lateral packing and low concentration of axial defects. The highest modulus fiber obtainable is one with highly oriented non-crystalline chains. LCP's are very good candidates for such endeavor.

By convention, heat-treatment is a process to stabilize the polymer chains and often, it also improves the fiber properties, for example, mechanical (tenacity and modules) and chemical. In most polymers, the as-spun fibers are first subjected to both drawing and heating. By careful manipulation of these processes the structure/morphology of the fiber can be changed and optimized to obtain the desired properties. To further improve the fiber properties, heat-treatment on the as-spun fibers are necessary. Thus, the fiber treatment information is of great importance and is normally patent protected or remains as proprietary information of the producers. In thermotropic LCP's drawing the as-spun fiber is not really viable since the amount of drawing is very limited. Thermal treatment is the only viable technique to improve the final property of the fiber.

This process is highly correlated to the change in molecular organizations even in the highly oriented stretched state. The fiber property can be greatly improved by the selection of an optimized heat-treatment condition. There are many variations of such treatments, in terms of temperature and exposure time, and multiple temperature/time steps, and/or fiber under tension. The mechanism for such behavioral changes upon heat treatment and resulted in such improvements is not fully understood. The choice of the heat-treating protocol is also of importance commercially because of the cost. Therefore, understanding of the mechanism at the molecular level to achieve the desired fiber property is important and also aids in eliminating the unnecessary portions of the heat-treatment cycle. A mechanical property comparison on the effect of annealing for CO and COTBP has been carried out by Nickolson et. al. [3].

We have followed, using WAXS and synchrotron SAXS techniques to examine the structure and morphology of two of our LCP (liquid crystalline polymer) polymer fibers, the co-polymer of CO (HBA/HNA (p-hydroxybenzoic acid/6-hydroxy-2-naphthoic acid), Vectran@) and COTBP, a polymer made up of HBA/HNA/BP/TA (BP- benzophenone, TA-terephalic acid) in the as-spun and heat-treated state. Vectran@ is available commercially from Ticona whereas COTBP is available as experimental material. We have also used thermal analysis (DSC, DMA and TMA) in order to provide more insight into the possible level at molecular behavior during heating. Both fibers have the typical liquid crystalline polymer structure, i.e., highly ordered structure across the fiber axis and aperiodic sequencing along the fiber axis. These results are consistent with previously determined structure [1, 2]. Close to the equator, a somewhat orthorhombic structure is observed and aperiodic structure on the meridian. The aperiodic nature due to sequencing along the fiber axis has been previously studied by modeling and x-ray diffraction. However, relatively little work has been carried out to describe the full structural behavior as a function of temperature and the consequence of heat-treatment.

SAMPLES:

Vectran@ fiber has both HBA/HNA (73/27, HBA= 4-hydroxybenzoic acid, HNA=2-hydroxy-6-naphthioc acid, also referred to as CO, Vectran@). Sample preparation is not the focus of this study and therefore will not be described here. COTBP is a variant of CO with two additional monomers, HBA/HNA/BP/TA (BP- benzophenone, TA-terephalic acid). The composition of COTBP has also been reported in earlier papers [3]. Both as-spun and heat-treated fibers of CO and COTBP were used in this investigation. The fiber samples are wound around a special

aluminum holder frame and the fibers are kept as parallel as possible and the sample thickness (bundle) is kept to be below 1 mm to avoid significant absorption.

EXPERIMENTAL:

X-ray diffraction experiments were carried out using the modified conventional Philip vertical goniometer utilizing copper Ka radiation. A diffracted beam analyzing crystal was used for energy discrimination. The diffractometer was modified so that the experiment can be carried out in transmission. The fiber axis can be rotated with respect to the scattering plane. At 0 degree angle, the fiber axis is perpendicular to the scattering, hence, the θ-2θ scan is equivalent to the equatorial scan and at 90° degree angle, meridonal scan is observed. Equator corresponds to the direction perpendicular to the fiber axis and meridonal scan corresponds to the scattering in the fiber direction. Steps of 5 degree interval for the fiber direction rotation are used. In this way, the Bragg condition is satisfied at all angles. By staying a particular 2θ location, the sample can be rotated in order to determine the angular spread, thus determine the Herman's orientation function. The degree of crystallinity is estimated from a plot derived by the summation of the 19 scans from 0 to 90 to cover the full fiber diagram. The spectrum can then be fitted to crystalline and amorphous component. The ratio of the crystalline peaks area to the total peak area is then defined as the degree of crystallinity.

The small angle x-ray scattering experiment is carried out using both the in-house system and one that is set up at X-11 beamline at NSLS (National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY.) pin-hole system. Because of the low scattering intensity, a direct detection CCD camera from Princeton Instrument is used. The accumulation was carried out by summation over several frames of data acquisitions.

Thermal analysis experiments which consist of DSC, DMA and TMA were carried out on the as-spun and heat-treated fibers. Perkin-Elmer DMA7 is used in the DMA mode heating and cooling rate of 3°/minute. For DSC experiments, TA Instruments 2100/900 is used with heating rate of 10°C/minute.

RESULTS AND DISCUSSION

The fibers chosen here for this study have been tested for tenacity and modulus. It is interesting to note that the as-spun CO has higher tenacity than COTBP whereas the modulus is more or

less similar. However, upon heat-treatment, an increase in tenacity can be observed in both fibers however the modulus of COTBP has increase drastically. It is also interesting to note that the heat-treated protocols in order to achieved maximum properties are also quite different between the fibers.

Table I: Physical properties of CO and COTBP

CO	As-spun	Heat-treated
Tenacity (g/d)	11	27
Modulus (g/d)	525	550
COTBP		
Tenacity (g/d)	8.5	21
Modulus (g/d)	520	880

Thermal analysis experiments are carried out on the LCP yarns for the as-spun and heat-treated Vectran. In the DMA experiments the a-relaxation was observed at ~100°C. A new dispersion peak was found at 65°C. It appears as a shoulder on the a-relaxation peak, and the origin of this process is not clear, because it was not seen during cooling and reheating. In the TMA experiments as shown in Figure 1, in the vicinity of 50°C, a relaxation can be observed and not seen during subsequent

THERMAL ANALYSIS

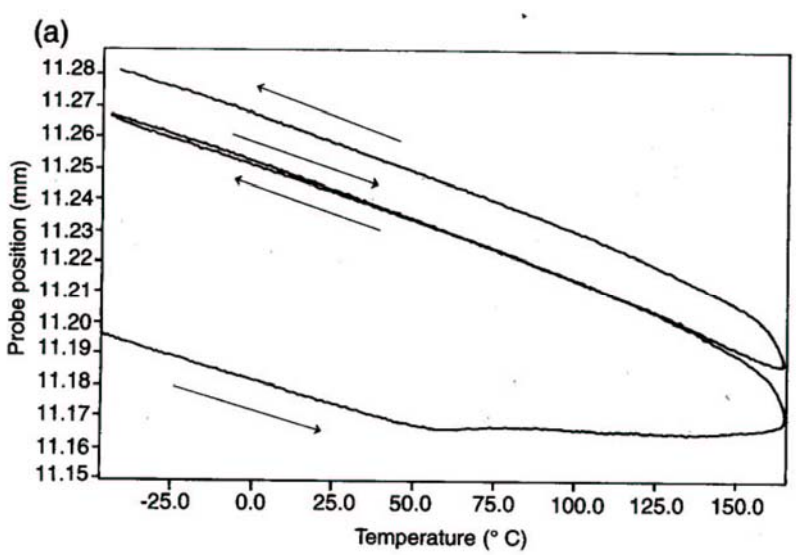

Figure 1: TMA traces of Vectran monofilament in a cyclic heating and cooling experiments [4]

heating and cooling. .

DSC measurements, as shown in Figure 2, indicate that at 100°C, the glass transition temperature of Vectran can be observed and melting occurs at about 280°C. The melting curve of Vectran often consists of two, barely visible MP1 and slightly more intense MP2. The magnitude of this peak suggests that this is unlike the conventional crystal melting. One can interpret the above result as having semi-ordered crystal structure of Vectran as having ordered, somewhat three-dimensional structure only along the equator and an aperiodic structure along the meridian. It can also be described as "paracrystalline" [5, 6] to describe this quasi-three-dimensional order, but no other unit cell has been observed. The DSC results clearly indicate that molecular ordering had occurred during heating up to the melting point. This ordering is unlike the conventional crystal building. The ordering is not observed upon continuing heating and cooling cycle. Hence, these results point to molecular chain ordering rather than chain folding to build crystals.

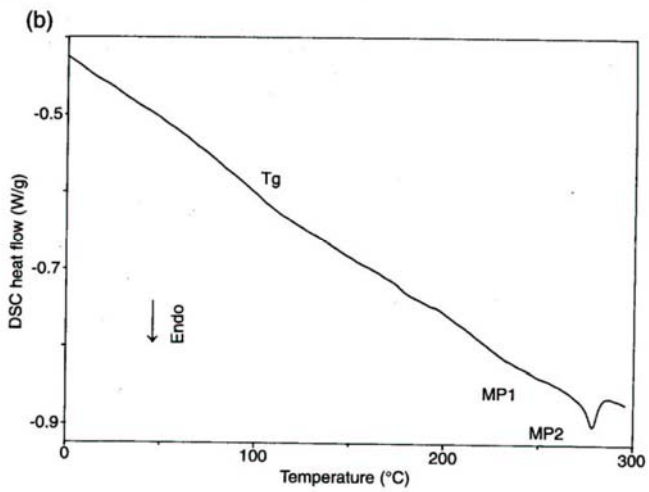

Figure 2: DSC traces of the as-spun fiber by Menczel et. al. [4]

The degree of crystallinity of LCP' is still very difficult to answer. There are discrepancies between the WAXS (wide angle x-ray scattering) and DSC (differential scanning calorimeter) measurements. Butzbach et al. [7] reported for HBA/HNA 58/42 sample, the degree of crystallinity is more than 60%. The crystals are far from perfect since the enthalpy and entropy of the transition are 10-20 times smaller than expected. Blundell [8], however, suggested that the degree of crystallinity should be lower and explained that the discrepancies between WAXS and DSC is because of the melting away of small micro-crystals that are too small to give sharp x-ray diffraction peaks.

X-RAY DIFFRACTION (WAXS)

The as-spun fibers are essentially at a metastable state indicating that they not fully organized. On the other hand, it is also possible due to the aperiodic nature of the polymer chains that fully molecular organized or crystallized structure cannot occur. Figure 3 shows the resulting 3-D fiber diffraction patterns for the as-spun and heat-treated CO and COTBP. Each diagram consists of 19 spectra. The spectrum in front corresponds to the data acquired at φ=0 is the equatorial scan and when φ=90 is the meridonal scan. The diagram for the as-spun CO and COTBP fibers are very similar. They both consist of a strong equatorial peak and probably a smaller shoulder peak on the right. The peak width refers to the crystal ordering which is about 30-40 Å

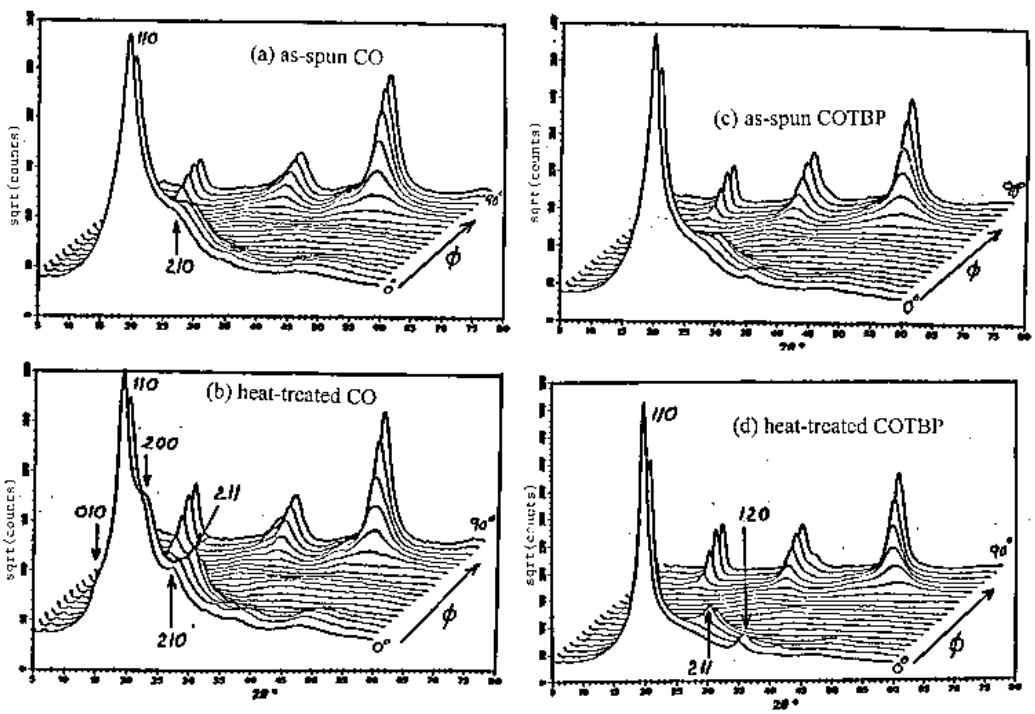

Figure 3: WAXS of as-spun and heat-treated CO and COTBP at ambient temperature

Differences were detected between the structural responses in the as-spun fibers as well as the heat-treated fibers as a function of temperature. A full extracted parameter describing the molecular structure is given in Table II. The d-spacing are extracted from peak positions, the crystallite size is estimated from the peak width and the orientation is determined by counting while rotating the fiber perpendicular to the scattering plane. The peaks close to the equator can be indexed to an orthorhombic structure while the higher angle meridonal peaks are due to the

aperiodic structure. Hence, they represent a quasi-order structure due to the random monomer sequencing along the chain and can be crudely indexed as 001 type reflections. The lattice parameters for the orthorhombic structure are roughly a=7.96 Å, b=5.69 Å and c=12.54 Å.

As indicated in Figure 3, the development of 3 additional peaks in CO and not COTBP can be observed in the heat-treated samples, indicating a much improved molecular organization in CO. The molecular organization of the as-spun CO is poor, being hindered by the random sequencing of the HNA and HBA monomer units along the chain. On heat treatment, in addition to apparent molecular weight increases, there are definite changes taking place in the molecular organization of the CO chains. The appearance of three new reflections suggests that CO chains are attempting to form a three dimensional crystal structure.

There are also shifts in the d-spacing in CO and not COTBP as listed in Table II suggesting a separation of the most electron dense region 110 planes. In addition, the degree of crystallinity increases from 39% to 48% for CO and 47% to 59% for COTBP upon heat treatment. There is only a small increase in the apparent crystallite size, measured from the (110) reflection. This increase is significantly more in COTBP than in CO. There is a slightly improvement in orientation function of COTBP than CO. There is no significant change in the meridonal scattering between the as-spun and heat-treated fiber, indicating that there is no changes in the monomer sequencing.

X-RAY DIFFRACTION (SAXS)

SAXS measurements were also carried out on the as-spun and heat treated CO fibers at ambient temperature. The results are shown in Figure 4. The as-spun fiber exhibits a horizontal streak through the origin which is normally attributed to needle shaped voids existing in the fiber with their long axes aligned parallel to the fiber direction, typically of LCP's. The SAXS patterns for the heat treated fiber are surprising because it is normally not expected and is only visible due to the high angular resolution used in the experiment. In addition to the lateral streak mentioned above, there is the appearance of an 'X' pattern. The angle of the "x" with respect to the fiber axis is about 10°. This can be reminiscent of the diffraction pattern from helical structures or sinuosity of the packing order [3] in CO. No such behavior is observed in COTBP.

Based on these findings it is postulated that the SAXS scattering is due to "organized kinks" at the molecular level being developed during heat treated CO fiber. The organization of these kinks

helps in the improvements of the molecular order as evidence in the appearance of additional off-diagonal peaks. Isolated kinks will not generate sufficient density contrast for SAXS to be observed. These kinks have to be synchronized and organized locally over 100-400 Å or larger in order exhibit the pattern as observed in SAXS. The HBA/HNA chains can form helical structures and can intertwine to form organized bundles. The in-plane kinks can synchronize forming regions of local coherence and the bending kinks can synchronize to form local regions where some of the tilted flat chain sections are parallel.

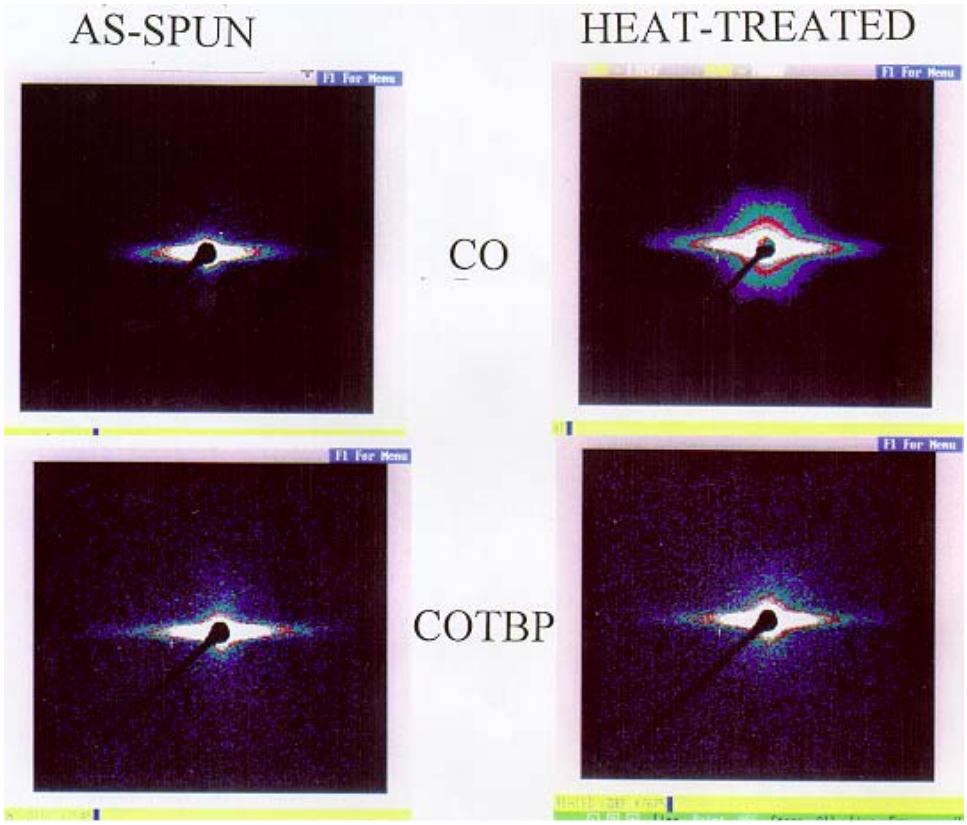

Figure 4: SAXS of as-spun and heat-treated CO and COTBP at ambient temperature

The organization of these kinks is due to the coming together of the phenyl rings along the molecular chains. There are four possible conformations of the two phenyl rings of HNA and two for the one phenyl ring of the HBA. With heat-treatment, in order to improve molecular order, conformation changes must occur by the rotation of the phenyl rings. During heat-treatment, these conformations readjust themselves to improve order which is the lowest energy level. Since there is no evidence of changes in the meridonal peak positions, it can be argued that there are no significant monomers sequencing re-arrangement or displacements along the chain axis. The rotations of the phenyl rings can be thought of as the rearrangement

of chain defects or chain entanglements, resulting in high density regimes.

SUMMARY AND CONCLUSIONS

Using the techniques of WAXS, SAXS and thermal analysis, an improved structural and morphological description at the molecular are being extracted. During heat-treatment of CO there is definite change in the organization at the molecular level attempting to form a three dimensional structure. As a consequence, the crystallinity increases. The most dense plane (110) expands and the (211) plane contracts to accommodate the formation of the unit cell. This is most likely due to the rotation of the phenyl ring resulting in the formation of "organized kinks". There is little improvement in the lateral order as measured by the crystallite size and there is no improvement in the orientation of the chains in the fiber.

The molecular organization of the as-spun COTBP already exhibits higher degree of crystallinity than CO, high order parameter is also observed. Upon heat treatment, similar to CO, the degree of crystallinity increases. The lack of additional peaks suggest that the molecular chains are attempting to come together without forming a three dimensional order. No new reflections are observed and there are no changes in the d-spacing. Hence, COTBP is not trying to form a three dimensional structure and the "organized kinks" are not observed during heat-treatment. All of this implies that COTBP tries to organize <u>outside</u> the unit cell rather than rotating the phenyl rings to form the kinks. Heat-treating COTBP merely straighten the chains which clearly improves the modulus. Because of the lack of kinks, the tenacity of COTBP is expected to be lower than CO. It is easier for the molecular chain of COTBP to slip than the organized kink chains of CO.

Since no significant changes in the x-ray peaks can be observed in the fiber direction (except for the first peak of as-spun CO) after heat-treatment, it can be concluded that the initial molecular response upon heating is in the chain rotations and inter-chains movements while the chain slippage along the fiber axis which contribute to the meridonial scattering are of the slower type.

SAXS experiments carried out on as-spun and heat-treated CO and COTBP, showed in addition to the normal void scattering, there is a “X” scattering which is postulated to be due to the formation of organized kinks in the heat-treated CO and not in COTBP. For COTBP, the molecules are straighter, due to the less about of HNA and do not segregate to form detectable

high density regions.

ACKNOWLEDGEMENT

The technical insight of the late Dr. Paul Harget is greatly appreciated.

REFERENCES

1] J. Blackwell and G.A. Gutierrez, *POLYMER 23*, 671 (1982)

[2] D. Hofmann, A.I. Schneider and J.Blackwell, *POLYMER* 35, 5603 (1994)

[3] T.M. Nicholson and I.W. Ward, *POLYMER* 39, 315 (1998)

[4] M. Jaffe, J. Menczel and W. E. Bessy, *Thermal Analysis of Polymeric Materials*, Academic Press, San Diego, CA 1981

[5] A.B. Erdemier, D. Johnson, I. Karacan and J.G. Tomka, *POLYMER* 29, 597 (1988)

[6] A. Biswas and J. Blackwell, *Macromolecules* 21, 997 (1988)

[7] G.D. Butzbach, J,H, Wendorff and H.J. Zimmermann, *POLYMER* 27, 1337 (1986)

[8] D.J. Bundel, *POLYMER* 23, 359 (1982)

Table II : XRD extracted parameters for as-spun and heat-treated CO and COTBP

CO AS SPUN CRYSTALLINITY = 39 %							CO HEAT TREATED CRYSTALLINITY 48 %						
PEAK	"d" in A	h	k	l	SIZE in A	f	PEAK	"d" in A	h	k	l	SIZE in A	f
							E	5.28	0	1	0		
E	4.55	1	1	0	31	0.942	E	4.63	1	1	0	39	0.941
							off E	4.51	1	1	1		
							E	4.04	2	0	0		
off E	3.35	2	1	1			off E	3.22	2	1	1		
E	3.23	2	1	0			E	3.26	2	1	0		
M	6.9		1st		51	0.933	M	6.94		1st		63	0.937
							H	3.42		2nd			
M	3.08		3rd		27	0.931	H	3.07		3rd		32	0.935
M	2.08		4th		48	0.905	M	2.09		4th		44	0.91

COTBP AS SPUN CRYSTALLINITY = 47%							COTBP HEAT TREATED CRYSTALLINITY = 59%						
PEAK	"d" in A	h	k	l	SIZE in A	f	PEAK	"d" in A	h	k	l	SIZE in A	f
E	4.49	1	1	0	60	0.96	E	4.49	1	1	0	74	0.974
off E	3.27	2	1	1			off E	3.29	2	1	1		
E	2.57	1	2	0			E	2.56	1	2	0		
M	6.07		1st		85	0.961	M	6.13		1st		92	0.971
H	3.24		2nd		49	0.939	M	3.26		2nd		65	0.949
							M	3.01		3rd			
M	2.09		4th		52	0.91	H	2.1		4th		61	0.934

E = equator , M = meridian