Reversible Crystal Deformation of Poly(tetramethylene terephthalate) Segments in Semicrystalline Segmented Poly(ether ester) Thermoplastic Elastomers

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ABSTRACT: Wide-angle X-ray scattering (WAXS) patterns of segmented poly(ether ester) fibers, which were made from poly(tetramethylene glycol) (PTMG) and poly(tetramethylene terephthalate) (PTMT), under tensile stress were studied to clarify the effect of the amorphous region on reversible crystal deformation of PTMT crystallites in the copolymers. The transition between the α and β crystal phases was observed around 800 Kg/cm^2 in tensile stress with various copolymers. The transition was not observed in PTMG rich copolymers in which the amorphous region was too soft to bear this level of tensile stress.

Introduction

Segmented poly(ether esters) are made up of an amorphous soft segment and a crystalline hard segment. Poly(tetramethylene glycol)[1−8] or poly(ethylene glycol)[22−25] are used as soft segments. Poly(tetramethylene terephthalate)[1−8,22−25] and poly(tetramethylene naphthalate)[26] are used as hard segments.

Segmented poly(ether ester) of poly(tetramethylene terephthalate) (PTMT) as a hard segment and poly(tetramethylene glycol) (PTMG) as a soft segment are commercially used together as a thermoplastic elastomer. It has gathered much attention.[1−8]

The copolymer's structure has been studied by several groups. Witsiepe[1] described its synthesis and physical properties. He studied wide-angle X-ray scattering (WAXS) patterns of drawn fibers of PTMT and PTMG copolymer and found the patterns of crystallites in the copolymer were the same as the α crystal phase of PTMT homopolymer. He concluded that the crystallized phase is essentially free of soft-segmented material (PTMG rich segments). Droescher and Regel[3] studied a WAXS pattern of cold extruded PTMT and PTMG copolymer and found it was consistent with the α structure of PTMT. Briber and Thomas[6] studied single crystals, grown from the melt in thin films. They found that the crystals exhibit (*hk*0) single crystal electron diffraction patterns, which index to the α crystal form of PTMT.

Poly(tetramethylene terephthalate) exhibits a reversible crystal transition between the α and β structures by mechanical deformation.[11] Koenig et al. studied the transition with infrared spectroscopy.[12] Raman spectroscopy was used to study the phenomena along with infrared spectroscopy by Ward and Wilding.[9] X-ray scattering was also used to investigate the phenomenon by Lando et al.,[13] Grasso,[14] and Ward et al.[15−17] The structure of α and β phase crystals were reported by several groups.[10,14,18−20] In the meantime, Ward et al.[21] reported the existence of a stable β form in oriented poly(tetramethylene terephthalate) specimens.

The existence of β phase structure in strained poly(ether ester) fibers and its relation to the mechanical properties of the fibers has not been reported yet. The reversible crystal deformation of poly(tetramethylene terephthalate) segments in PTMG−PTMT copoly(ether ester) and its relation to the tensile properties is discussed in this paper.

Experimental Section

Materials. Samples of segmented poly(ether ester) of PTMT and PTMG were kindly supplied by Dr. Ronald E. Uschold of Du Pont E. I. de Nemous & Co. PTMG contents in weight percent, melting point (M_p) by differential scanning calorimetry (DSC), and melt index values (MI) were supplied with the samples and are compiled in Table 1. They were prepared by polycondensation of PTMG, dimethyl terephthalate, and 1,4-tetramethylenediol as described by Witsiepe.[1]

PTMT homopolymer was kindly supplied by Mr. T. Sugita and Mr. T. Katsuura of Mitsubishi Chemical Corp.

Sample Preparation. Sample pellets were dried at 120 °C under vacuum overnight. Sample pellets were put in a ram extruder and melted at 245 °C and then extruded into a fiber, which was about 1 mm in diameter. With the use of clamps, the fibers were stretched 275% at room temperature to orient the crystallites. The fibers were then annealed under vacuum overnight to enhance crystallization under tension. The annealing temperature was 150 °C for the copolymers and 200 °C for the PTMT homopolymer. The oriented and annealed fibers were used for the measurement of WAXS and tensile properties.

Wide-Angle X-ray Diffraction (WAXS). Wide-angle X-ray scattering was measured with specimens under various strains. X-ray photographs were taken under vacuum with a Torrid camera. The sample strand was mounted in a clamp and set perpendicular to the X-ray beam. Nickel filtered Cu Kα radiation (wavelength = 0.154 18 nm) was used. Three Kodak DFE films were exposed at the same time. Exposure time was varied from 12 to 30 h according to the diameter of the sample. The distance between the sample and the films was calibrated with CaF_2, which was dusted on the samples. The photographs were digitized and analyzed on an NEC PC9801ES computer equipped with a Sharp JX320 color image scanner and a JX32F3 transparency reader unit. The maxi-

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Table 1. Mechanical Properties and Crystalline Phase under Strain of Oriented PTMT/PTMG Poly(ether ester) Fibers

	for given sample name							
	PTMT (homo)	LRI995	LRI996	LRI999	LRI1000	LRI1001	LRI1002	LRI1003
PTMG								
wt %	0	19	27	41	51	57	64	64
M_w		1000	1000	1000	1000	1000	1000	2000
melt index, g/10 min		18	10	2	21	21	14	15
melting point, °C	225	218	207	198	186	177	165	193
	Crystalline Phase Under Strain							
elongation								
0%	α	α	α	α	α	α	α	α
20%	*β*	*β*	α + *β*	α	α	α	α	α
40%		*β*	*β*	α + *β*	α	α	α	α
80%		*β*	*β*		α	α	α	α
160%			*β*		*β*			α
300%								α
tensile modulus, Kg/cm^2	25200	6700	3800	1900	1200	1100	600	400
tensile strength, Kg/cm^2	1640	1700	1570	1610	1030	860	690	650
elongation at break, %	22	36	49	233	105	166	267	313
stress at 40% strain, Kg/cm^2	2070	1750	1460	700	600	360	180	120
	Estimate Values at Transition							
elongation, %	8	15	20	40	120	no *β*	no *β*	no *β*
stress, Kg/cm^2	800	700	700	700	1000	no *β*	no *β*	no *β*

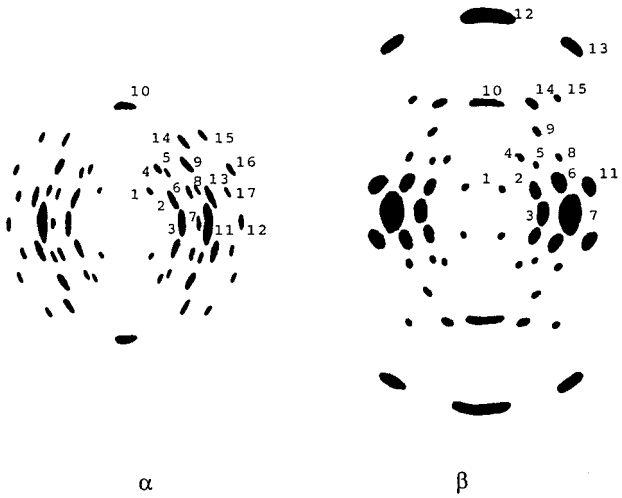

Figure 1. Schematic diagrams of the fiber diffraction patterns of the α and *β* phases of PTMT.[13,14,17] Area of reflections is not indicative of relative intensities. Inset numbers indicate assignments of reflections in Table 2.

Table 2. Indices for Reflections of α and *β* Phases of PTMT

reflection no. in Figure 1	Indices					
	α phase			*β* phase		
	h	*k*	*l*	*h*	*k*	*l*
1	$\underline{0}$	0	1	0	$\underline{0}$	1
2	$\bar{1}$	0	1	0	$\bar{1}$	1
3	1	0	0	0	1	0
4	$\underline{0}$	0	2	$\underline{0}$	0	2
5	$\bar{1}$	$\underline{0}$	2	$\bar{1}$	0	2
6	1	$\bar{1}$	1	$\bar{1}$	0	1
7	1	$\bar{1}$	0	1	$\underline{0}$	0
				$\underline{1}$	$\bar{1}$	0
8	1	$\underline{0}$	1	$\bar{1}$	1	2
9	1	$\bar{1}$	2	$\underline{0}$	0	3
10	0	$\bar{1}$	4	$\bar{1}$	$\underline{0}$	4
11	0	$\underline{1}$	0	$\bar{1}$	$\bar{1}$	1
12	2	$\bar{1}$	0	$\underline{0}$	$\bar{2}$	6
				$\bar{1}$	0	6
13	$\bar{1}$	1	1	$\underline{0}$	$\underline{0}$	6
14	$\bar{1}$	0	3	$\bar{1}$	$\bar{1}$	4
				0	$\bar{1}$	4
15	1	$\bar{1}$	3	0	0	4
16	1	$\bar{1}$	2			
17	0	1	1			

mum resolution of the digitizer is 600 dots/inch (dpi) with 256 steps in intensity. A resolution of 75 dpi was assumed in this study.

Tensile Properties. Tensile properties were measured with a Toyo-seiki Storograph R2 equipped with a NEC PC9801DX data processor. Sample displacement was 32 mm, and the rate of deformation was 2 mm/min (1.04×10^{-3} s^{-1}). Measurements were performed under ambient condition of 23 °C and 50% relative humidity.

Results and Discussion

Results of the tensile measurements, crystal phase assignment, and data, which were supplied with the samples, are compiled in Table 1. The phase assignments in the table are the dominant crystal structure in the samples.

Assignment of the Crystal Structure of PTMT. Figure 1 shows WAXS patterns of the α and *β* crystal phases of PTMT homopolymer.[13,14,18] Inset numbers indicate assignments of reflections, which are listed in Table 2.[14,18] Figure 1 is drawn and Table 2 is compiled according to the references. The Miller notation of $(0,\bar{1},0)$ is used for reflection (zero, minus 1, zero) in this paper. There are several differences between them. The following three differences were used to decide if α or *β* crystals were present.

The first difference between the two patterns is the existence of a $(0,\bar{1},0)$ reflection on the layer line of the α phase. The *β* crystal does not show any reflection in this region. Figure 2 shows an intensity readout of WAXS photographs on the layer line of oriented and annealed fibers which was made from PTMT homopolymer under various strains. Reflections at no strain fit the descriptions of the α crystal structure.[18−20] The WAXS pattern at 30% strain showed no $(0,\bar{1},0)$ reflection and was assigned to *β* crystal. In addition, excess strain causes disorder and deformation of the *β* structure. The WAXS pattern at 50% strain shows this effect. When the oriented fiber of PTMT homopolymer is stretched to this level, the crystal structure does not return to the α structure upon release but remains in the *β* structure. This phenomenon was also observed by Ward et al.[21] and attributed to weak coupling with the surrounding amorphous region.

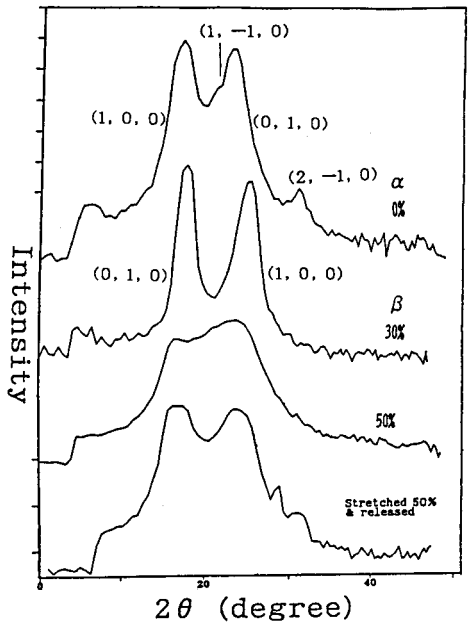

Figure 2. WAXS on the layer line: PTMT homopolymer, stretched 0, 30, and 50% and strained and released.

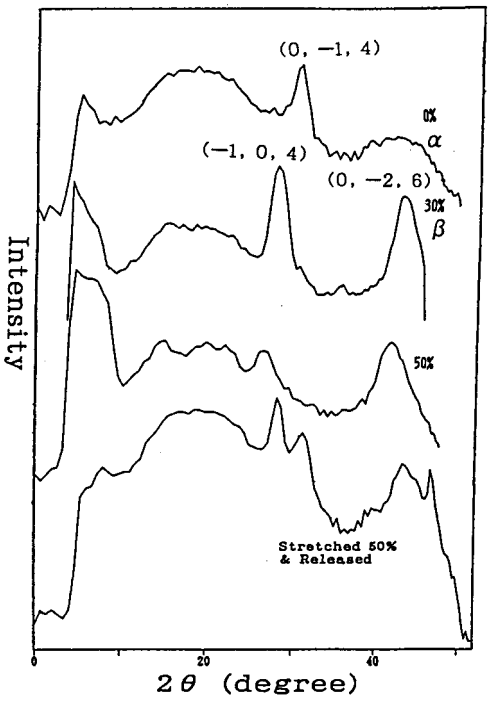

Figure 3. WAXS on the meridional line: PTMT homopolymer, strained 0, 30, and 50% and strained 50% and released.

The second difference is a *d* spacing on the fourth layer line. Since the *c*-axis of the β phase is about 8% longer than α crystals, this can be a good indication for assignment of the crystal phases. The $(0,\bar{1},4)$ reflection of the α phase and the $(\bar{1},0,4)$ reflection of the β phase are sufficiently near the meridional line to be used for the comparison. This method was utilized by Ward et al.[15] to show the reversible crystal deformation. In addition, the β phase shows a $(0,\bar{2},6)$ reflection on the meridional line, whereas the α crystal does not show a reflection in this region. WAXS on the meridional line of PTMT homopolymer is shown in Figure 3. Reflections around 43° are observed with specimens stretched 30 and 50% and released after 50% stretched specimens.

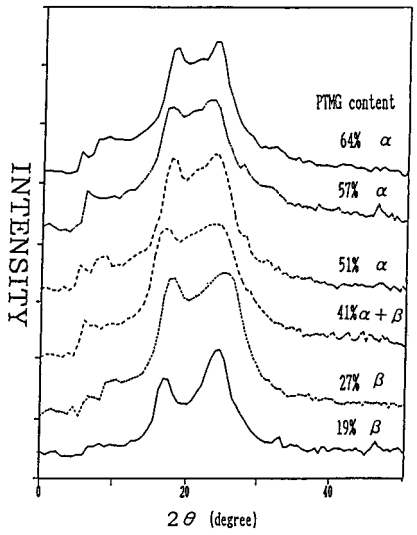

Figure 4. WAXS on the layer line at 40% strain: PTMG/PTMT poly(ether esters), PTMG content 64, 67, 51, 41, 27, and 19%.

These reflections are assigned to the $(0,\bar{2},6)$ reflection of the β crystal. The $(0,\bar{1},4)$ reflection of the α crystal and the $(\bar{1},0,4)$ reflection of the β crystal are observed at 32 and 28°, respectively. The larger *d* spacing of the $(\bar{1},0,4)$ reflection of the β phase was observed with the $(0,\bar{2},6)$ reflection of the β phase. The $(\bar{1},0,4)$ and $(0,\bar{2},6)$ reflections of the 50% stretched sample are broader than in the other specimens. This suggests that the crystal structure of the specimen is somewhat disordered. PTMT homopolymer without tension (0%) is assigned to the α phase. Samples, which were stretched 30% and released after 50% stretch, are assigned to the β phase. These results agree with the assignments from the layer data.

The third is a difference on the first layer line. The α crystal has (0,0,1), $(\bar{1},0,1)$, $(1,\bar{1},1)$, (1,0,1), and $(\bar{1},1,1)$ reflections on the first layer line near the meridional. The β crystal has the (0,0,1), $(1,\bar{1},1)$, $(\bar{1},0,1)$ and $(\bar{1},\bar{1},1)$ reflections in a similar region. The disappearance of the $(1,\bar{1},1)$ and (1,0,1) reflections of the α crystal and the emergence of the $(\bar{1},0,1)$ reflection of the β phase is a notable change on the first layer line during crystal transition. Existence and disappearance of these reflections were utilized to confirm the assignments.

Effect of PTMG Content in PTMG/PTMT Poly(ether esters) on the α to β Crystal Transition of PTMT Crystallites. When a PTMT sample fiber is strained, the PTMT crystallites that embed in the amorphous region are stressed. The increase of tensile stress on the PTMT crystallites in the sample fibers cause the α to β crystal transition. The increase of PTMG content in PTMG−PTMT copoly(ether esters) decreases the tensile modulus of the oriented fibers. Thus, the stress applied to the PTMT crystallites in the specimen at a given strain of the sample fiber decreases with the increase of the PTMT content. Though the increase of PTMG content decreases the crystallinity of PTMG−PTMT copolymers, the structure of PTMT crystallites is the same. While PTMG is in amorphous region, the PTMG to PTMT ratio in the amorphous region affects the tensile modulus of the amorphous region. The increase of PTMT in the amorphous region of less crystalline PTMG−PTMT copolymer affects the stress on the PTMT crystallites in the sample fibers by changing the tensile modulus of the amorphous region.

Table 3. Meridional *d* Spacings

			(0,$\bar{1}$,4)/($\bar{1}$,0,4)		0,$\bar{2}$,6		
sample name	PTMG, wt %	elongation, %	2θ, deg	*d* spacing, Å	2θ, deg	*d* spacing, Å	assigmt
LRI995	19	40	28.3	3.2	47.0	1.9	β
LRI996	27	40	28.5	3.1	43.8	2.1	β
LRI999	41	20	31.6	2.8			α
		40			43.5	2.1	β
LRI1000	51	40	31.3	2.9	43.3	2.1	α
		80	31.2	2.9	43.3	2.1	$\alpha + \beta$
		160			43.2	2.1	β
LRI1001	57	40	31.6	2.8			α
LRI1002	64	40	31.7	2.8			α
LRI1003	64	20	32.1	2.8			α
		40	31.6	2.8			α
		80	32.1	2.8			α
		160	31.7	2.8			α
		300	32.9	2.7			α

The effect is not significant compared to the effect of PTMG on the amorphous content. The effect of increasing PTMG content on the stress on PTMT crystallites is the same as decreasing strain on a sample fiber of PTMT homopolymer. The phenomenon was studied through WAXS photographs by the methods described in the previous section.

Figure 4 shows the WAXS on the layer line of six samples with various PTMG contents (19, 27, 41, 51, 57, and 64 wt %; M_w of PTMG is 1000) at 40% strain. With the increase of the PTMG content, the (0,$\bar{1}$,0) reflection of the α crystal became more apparent. This suggests an increase of the α crystal content at constant tensile strain in these sample fibers. The (0,$\bar{1}$,0) reflection of the α crystal almost disappeared with 27% PTMG content. The sample with 41% PTMG showed a mixed pattern of the α and β phases. Therefore the α to β transition under 40% tensile strain occurs at approximately 41% PTMG content.

The 2θ angles of WAXS on the meridional of six samples with different PTMG contents at various strains are compiled in Table 3. *d* spacing data calculated from them are also listed in Table 3. Data taken from the same X-ray photographs used for Figure 4 are included in Table 3. The α to β crystal transition is observed upon 40% strain near a PTMG content of 41 wt % and upon 80% strain at a PTMG content of 51 wt %. These results agree with those of the layer line.

Sample fibers with lower modulus need larger strain for the α to β transition. These results suggest that a certain amount of stress is necessary for the α to β transition of PTMT crystallites.

Reversible α and β Crystal Transition of PTMT Crystallites in PTMG−PTMT Copoly(ether esters). The specimens of PTMG−PTMT copoly(ether esters), which were studied in this paper, showed a reversible α to β crystal transition when the β structure became observable after the stretch. The deformed β structure, which was observed in PTMT homopolymer, was not observed with these copoly(ether esters). These phenomena were observed with specimens which contain 19−51 wt % PTMG. The example of copoly(ether ester) with 51 wt % of PTMG is described below in detail.

Figure 5 shows WAXS on the layer line of a specimen which contains 51 wt % PTMG of molecular weight 1000 at various strains (40, 80, and 160% and released after 160% strain). The α to β transition occurs between 80 and 160% strain, which is much larger than the transition strain of PTMT homopolymer (less than 30%). Even with 160% strain the β crystal structure was not deformed as observed with PTMT homopolymer at

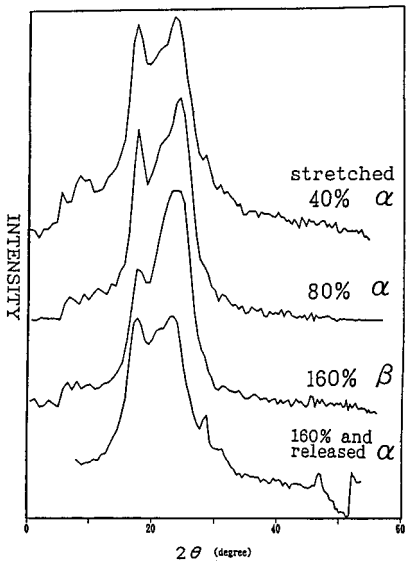

Figure 5. WAXS on the layer line: PTMG/PTMT poly(ether esters) with 51% PTMG, strained 40, 80, and 160% and released.

strains over 50%. The α to β transition of the copoly(ether esters) was reversible. The specimen which contained the β crystal went back to the α phase when the strain was released after 160% stretch. This might be because of the soft amorphous region of the copolymers which cannot sustain enough stress to maintain the β crystal structure. Under similar conditions the PTMT homopolymer retains enough residual stress to maintain the β structure.

Data on the first layer line agrees with the assignment made using the layer line. The ($\bar{1}$,1,1) reflection of the α crystal was observed in all but the sample with 160% strain. Therefore samples with 40% strain and 80% strain and released samples after 160% strain have primarily α crystallites. The sample under 160% strain has β crystallites.

Soft specimens which contain a large amount of PTMG do not show the β crystal even with large strain. As is shown in Table 1, the sample fibers with more than 57% PTMG (LRI1001, LRI1002, and LRI1003) did not show the β phase upon stretching. The specimen with 64% PTMG showed an α pattern even when it was strained up to 300%. The strain is more than 10 times larger than the strain at the transition point of PTMT homopolymer. In addition, the sample containing 64% PTMG with molecular weight 2000 showed the largest elongation at a break of 313%. It could be stretched up

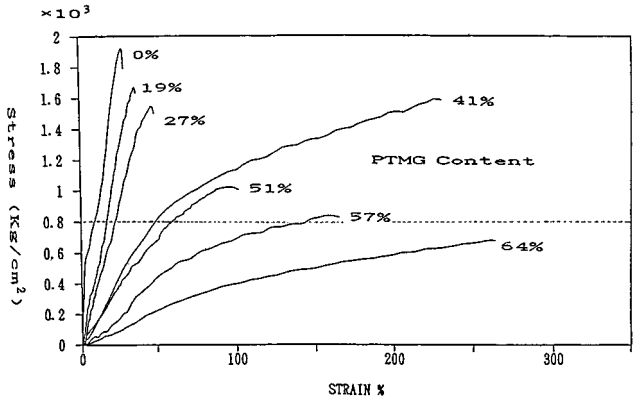

Figure 6. Stress−strain curves of PTMG/PTMT poly(ether esters). PTMG content: 0, 19, 27, 41, 51, 57, and 64%.

to 300%. Its high content of PTMG and high molecular weight (low melt index) made the sample the softest thus withstanding the largest tensile strain. Other samples (LRI995−LRI1002) contain PTMG with a molecular weight of 1000.

Stress−Strain Curves and Tensile Stress at the α and *β* Crystal Transition of PTMG−PTMT Copoly(ether esters). The values of the tensile stress at the transition were about 800 Kg/cm^2 and did not vary much with PTMG content. As the tensile modulus decreases with the PTMG content, tensile strain at the transition is increased with increasing PTMG content. Since both the α and *β* crystal structures are the same in PTMT homopolymer and PTMG−PTMT copoly(ether esters), the tensile stress which is necessary for the α to *β* transition is the same in these polymers. Estimated tensile strain and stress at the α to *β* transition of PTMG/PTMT copolymer specimens are listed in Table 1. Stress−strain curves of oriented and annealed fibers of PTMT homopolymer and PTMG−PTMT copolymers are shown in Figure 6.

Tensile strain (elongation) at the transition was defined as a value at which the α and *β* crystal contents in the specimen is each 50%. This was estimated from the α and *β* assignment from WAXS data in Table 1 with the following two criteria. First, if the WAXS photograph on Table 1 showed both α and *β* crystals, the strain value of the photograph was selected as the value at the transition. Second, if the WAXS photographs in Table 1 showed only an α or a *β* crystal, respectively, the mean value between the α and *β* photographs was adopted as the value at the transition. The tensile stress at the transition was determined from stress−strain curves by reading stress values at the strain determined as described above.

Conclusion

PTMT crystallites showed similar α to *β* crystal transition both in PTMT homopolymer and PTMG−PTMT copoly(ether esters) with less PTMG segments. The transition occurred when the stress exceeded 800 Kg/cm^2 irrespective of PTMG content. When PTMG content is high, the tensile stress cannot exceed 800 Kg/cm^2 even at high strain. Then the α to *β* crystal transition does not occur. The stable *β* form, which was observed in PTMT homopolymer, was is not observed in the copolymers.

A question remaining is that the stress at the α to *β* crystal transition might be lower than 800 Kg/cm^2 if there is stress relaxation creep during X-ray exposure under stress. Bulk specimens without orientation such as injection molded test pieces show necking at 500 Kg/cm^2.[27,28] If the α to *β* transition occurs at this stress, then, given the double yielding in PTMT, the yield would be occurring in the crystalline regions before the amorphous regions.

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