Crystalline, Thermal, and Mechanical Properties of the Polyester of α-Methyl-α-n-propyl-β-propiolactone

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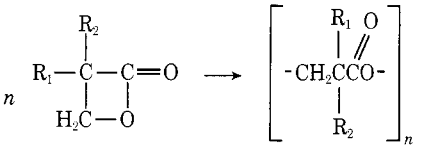
ABSTRACT: Homopolyesters prepared by anionic ring-opening polymerization of α-methyl-α-n-propyl-β-propiolactone using tetrahexylammonium benzoate as initiator have been prepared. Because a D,L monomer mixture was used, the presence of crystalline order as found by X-ray diffraction was interpreted in terms of isomorphous substitution or eutectic behavior corresponding to an equimolar mixture of two crystallizable comonomers. In either case, an atactic structure is implied and a relatively low degree of crystalline order was found. Two crystalline polymorphs superposed their diffraction spots in the fiber diagram of stretched films and the fiber repeat distances of 4.7 and 5.9 Å suggest planar zigzag and 2_1 helical conformations. The effect of stretching was to encourage the transformation of the 2_1 form into the extended chain polymorph. Mechanical properties showed both stress softening and stress hardening behavior depending on the extent of cyclic deformation. Thermal studies revealed multiple melting peaks with the concentration of higher melting material being favored by stretching. The results are interpreted in terms of a domain structure of "hard" and "soft" regions corresponding to 2_1 helix and extended chains, respectively.

The synthesis of polyesters from α-substituted β-propiolactones is well known.[2a] The ring-opening polymerization reaction can be carried out by either anionic or cationic mechanisms to form linear polymers of high molecular weight according to the following reaction



α-substituted poly(β-propiolactones)

Poly(β-propiolactone), the parent polymer of this series, has been shown to exist in the solid state in two crystalline forms.[2b,3] One form is a 2_1 helix conformation, the other, a planar zigzag conformation. The latter can be transformed into the former by slow heating to 65°. The zigzag form predominates in films cast from chloroform solution by slow evaporation, while the helical form predominates upon rapid evaporation of the solvent.

Another monomer of this series α,α-dimethyl-β-propiolactone, commonly called pivalolactone, yields a polyester (PPL) which is also reported to have two crystalline forms, again a 2_1 helix[4] and a planar zigzag conformation.[5] The latter is formed as a result of high-speed stretching during melt spinning of the polymer.[5]

A number of polymers of other α,α-disubstituted β-propiolactones have been reported to be crystalline,[2a] including many cases in which the substituents R_1 and R_2 are different (*i.e.*, the repeating units have an asymmetric structure) although the starting monomer was a D,L mixture. This paper reports on the polyester prepared by the anionic ring-opening polymerization of α-methyl-α-n-propyl-β-propiolactone (MPPL), $R_1 = CH_3$ and $R_2 = CH_2CH_2CH_3$.

Experimental Section

MPPL monomer was prepared[6] from 2-methyl-2-n-propyl-1,3-propanediol as the starting material. This compound was reacted in several steps to form the ω-bromocarboxylic acid, and ring closure was effected in an aqueous, alkaline medium. No attempt was made to resolve the monomer into its optical isomers, and all polymerizations were performed with the racemic mixture. No optical activity was observed for the polymer.

The polymerization reactions were carried out in tetrahydrofuran that had been dried by refluxing over sodium. The monomer was purified by distillation over calcium hydride. The initiator used in all polymerization reactions was tetrahexylammonium benzoate (Eastman Kodak 10355).

Films of purified polymer were prepared either by compression molding at 70° at low pressure on a Carver press, or by solvent casting from a tetrahydrofuran solution. X-Ray diffraction patterns of the films were recorded at room temperature, *in vacuo*, in a flat film camera using Ni-filtered Cu Kα radiation. X-Ray fiber diagrams were similarly recorded from film samples that had been stretched 600% while heated to near the softening point. X-Ray diffractometer scans were obtained using a General Electric XRD-5 instrument at a scan speed of 0.2°/min.

The thermal behavior of the polymer was studied using a Perkin-Elmer Model IB differential scanning calorimeter (DSC). Stress-strain properties of the films were evaluated on an Instron table model "TM" tensile tester at a stretch rate of 1 in./min at 35°, using a gauge length of 1 in.

The resulting linear polyester had the expected carbonyl absorption band at 1740 cm^{-1} and elemental analysis corresponded to that expected for the repeating unit of the linear polyester of high molecular weight. The number average molecular weights obtained by anionic polymerization agreed with those expected from the initiator-to-monomer ratio for a polymerization reaction free of transfer and termination reactions. Molecular weight distribution analysis was performed by gel permeation chromatography using a Waters Associates Model 200 instrument. The analysis was done in tetrahydrofuran solution at 25°, at a "flow rate" of 1 in./min. The polymer samples were dissolved in degassed tetrahydrofuran (0.25% w/v) and filtered under nitrogen before injection. The analysis verified that the polymers had a narrow molecular weight distribution. The data are given in Table I.

No optical activity was found over the wavelength range 6000–3000 Å, indicating that no stereoelectivity occurred during polymerization. The resulting polymer, therefore, is either a random D,L copolymer or a stereoblock copolymer. A physical mixture of polymer molecules which are optical antipodes is also conceivable.

Crystal Structure and Conformation

Both pressed and solvent-cast films yielded well-defined X-ray powder patterns (Figure 1) which were similar in appearance. The 2θ values calculated from the powder pattern (Figure 1) are collected in the first column of Table II. After stretching the film samples at the appro-

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(1) (a) Université de Montreal; (b) University of Massachusetts.

(2) (a) R. Thiebout, N. Fisher, Y. Etienne, and I. Coste, *Ind. Plast. Mod. Elastomers*, 14, 1 (1962). (b) K. Wasai, T. Saegusa, and J. Furakawa, *Kogyo Kagasu Zasshi*, 67, 601 (1964).

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(5) F. W. Knobloch and W. O. Statton, U. S. Patent 3,299,171 (1967), E. I. DuPont de Nemours Co.

(6) H. K. Hall, *Macromolecules*, 2, 488 (1969).

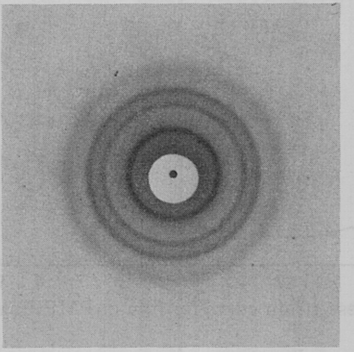

Figure 1. X-Ray powder diagram of poly(D,L-α-methyi-α-*n*-propyl) (PMPPL) propriolactone film.

Table I
Molecular Weight Analysis by GPC for Polymerized MPPL

Sample	$\overline{M}_n$ (Calcd)	$\overline{M}_n$ (Obsd)	Peak Width GPC (Counts)	$\overline{M}_w/\overline{M}_n$
A	26,000	25,000	3.6	1.13
B	96,000	95,600	3.5	1.10
Standard polystyrene		51,000	3.2	1.02

Table II
Comparison of X-Ray Diffraction 2θ Values in Degrees as a Function of Stretching with Values for Reference Conformations

2θ Values		Peak 2θ Values from Stretching Expt				
2_1 Helix[a]	Planar Zigzag[b]	A	B	C	D	E
	8.78				8.85	8.7
9.45		9.15	9.2	9.2		
	11.8				11.0	11.5
14.7		14.3	14.4	14.5	14.5	14.7
17.5	17.5	17.1	17.2	17.3	17.2	17.1
20.2						
	21.0	21.1				
	22.5					

[a] As measured from powder patterns. [b] Taken from Table III.

priate softening temperature (near 70° in hot water), two sets of layer lines could be observed (Figure 2): one corresponding to the linear zig-zag form with a fiber repeat distance of 4.74 Å and the other to a polymorph with a fiber repeat distance of 5.9 Å, which is very similar to the reported[4,5] fiber repeat of the 2_1 helix form of poly(pivalolactone) (5.96–6.02 Å) and is probably to be associated with a conformation analogous to the 2_1 helix of the latter. It has been proposed that the 2_1 helical conformation of all polymer chains with the β-propriolactone backbone have about the same fiber repeat independently of the nature of the substituents at the α position.[7] This would be similar to the isoconformationalism of crystalline proteins (the α helix) but without the aid of intramolecular hydrogen bonds. No doubt the latter situation is responsible for the ease with which the apparent dimorphic transformation (helix → zigzag conformation) is induced in these polyesters whereas proteins generally require steam stretching.

The layer lines associated with the planar zigzag form, observed after film stretching, were sharply oriented and maintained their orientation even when the stress was relaxed; the layer lines for the presumed helical form were oriented and most visible when no stress was applied. After elongation and stress release, the film strips would contract somewhat, and the intensity of the helix reflections would increase with time. Thus the two sets of reflections, although appearing on the same fiber diagram, were readily distinguishable (Figure 3).

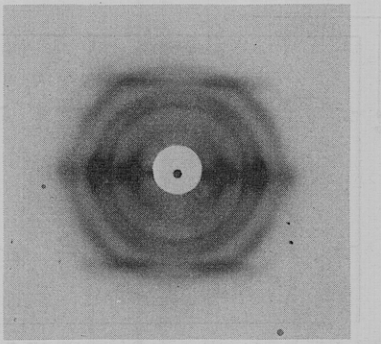

Figure 2. Fiber diagram of PMPPL. The polymer film was stretched about 600% at 60° and quenched to room temperature.

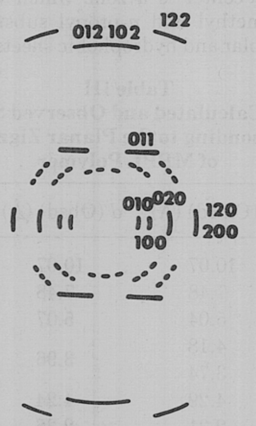

Figure 3. Schematic representation of fiber diagram in Figure 2: full lines correspond to reflections of the planar zigzag form and broken lines are reflections of the 2_1 helical conformation.

A comparison of the measured 2θ values of the X-ray powder diagrams (Table II), with those of the fiber diagram, indicates that the observed powder diagram is generated by a crystalline form other than the zigzag chain. This other crystalline form is obviously the 2_1 helix since the fiber repeat corresponding to the dotted reflections in Figure 3 index for a value of 5.9 Å.

From the reflections of the planar zigzag crystalline form of the MPPL polyester, a unit cell was calculated which corresponds to an orthorhombic structure having the following cell parameters: a = 7.48 Å, b = 10.1 Å, and c (fiber axis) = 4.7 Å. The observed and calculated reflections are shown in Table III.

An orthorhomic cell with the dimensions a = 4.48 Å, b = 7.73 Å, and c = 4.76 Å has been reported[8] for the planar zigzag form of poly(β-propiolactone). The cell dimensions of the zigzag form of poly(pivalolactone) have not been reported because of insufficient data although a fiber repeat of 4.76 Å has been reported.[5]

The 012 and 102 reflections corresponding to predicted interplanar spacings of this unit cell were observed at 2.24 and 2.36 Å in diffractograms of films inclined to the X-ray beam at or near the Bragg angle of the reflections. However, the meridional reflections (001) and (002) were never observed even for the tilted film, although layer line

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(7) J. Cornibert and R. H. Marchessault, *J. Mol. Biol.* 71, 735 (1972).

(8) H. Tadokoro, M. Kobayashi, H. Yochidome, K. Tai, and D. Makino, *J. Chem. Phys.*, 49, 3359 (1968).

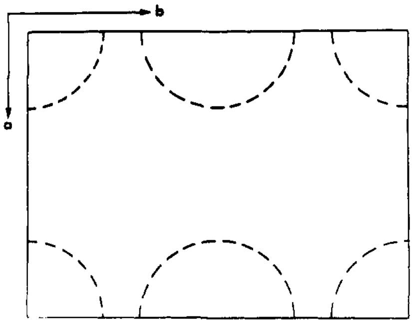

Figure 4. Simple representation of the unit cell base plane corresponding to the planar zigzag conformer of PMPPL. The center of each broken line circle is a lattice point for a chain axis and the empty space in the center is a zone which would preferentially accommodate the methyl and *n*-propyl substituents thereby allowing alternating polar and hydrophobic sheets.

Table III
Comparison of Calculated and Observed Spacings for the Unit Cell Corresponding to the Planar Zigzag Conformation of MPPL Polymer

hkl	*d* (Calcd) (Å)	*d* (Obsd) (Å)	2θ (Obsd)
(010)	10.07	10.07	8° 47′
(100)	7.48	7.48	11° 50′
(020)	5.04	5.07	17° 30′
(120)	4.18	3.96	22° 28′
(200)	3.74		
(011)	4.29	4.24	20° 58′
(012)	2.31	2.36	38° 07′
(102)	2.26	2.24	40° 19′
(122)	2.06	2.05	44° 02′

streaking is present on the first layer line. Using the flotation method, the measured density was 1.07 g/cm^3 compared to 1.20 g/cm^3 for the theoretical value of this crystalline form when the unit cell contains two monomer units with a molecular weight of 128. Because the fiber repeat period of 4.7 Å corresponds to one extended repeating unit, there must be two polymer chain segments in each unit cell.

The distribution of the X-ray intensities on the equator suggests the positions shown in Figure 4 for the two polymer chain segments. This arrangement is essentially a sheet-like structure which may involve alternating hydrophobic and polar sheets as in the β-polypeptide structures but there is unsufficient evidence to firmly establish the chain packing.

Because this product was prepared from a D,L monomer mixture and the resulting polymer was not optically active, it must be considered to be an equimolar copolyester of the two asymmetric monomer units which are optical antipodes. In such cases, the polymer is usually amorphous unless crystallization can result from one of the following conditions. (a) The D and L repeating units are arranged in stereoblocks which are long enough to crystallize separately. (b) The D and L repeating units are isomorphous in the unit cell, or they crystallize separately as a result of statistical sequences of predominantly D or L configurations. (c) A syndiotactic structure, *i.e.*, alternating D and L residues are present in the chain. The results of this study suggest that the D and L repeat units are isomorphous, at least in the planar zigzag unit cell. Of the three simplest possible stereostructures for the MPPL polyester; syndiotactic, isotactic, and atactic, the X-ray fiber data on the stretched sample required the elimination of the syndiotactic case. The fiber repeat period of the planar zigzag form, 4.74 Å corresponds precisely to one repeating unit and a syndiotactic polymer with this arrangement must necessarily yield a fiber repeat which contains at least two repeating units.

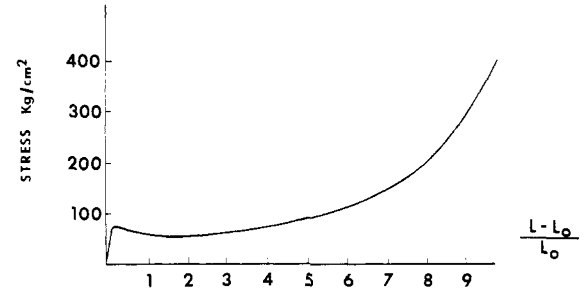

Figure 5. Stress-strain curve for film of PMPPL tested at 35° and 1 in./min.

Of the other two possible structures, the atactic form was selected on the basis of the simplicity of the unit cell (planar zigzag form) which completely lacks the elements of symmetry which are characteristic of the various isotactic structures so far repeated.[9] Furthermore, the first layer line shows a characteristic streaking without resolved diffraction spots. This suggests a lack of longitudinal order and because this layer line corresponds to spacings of ~4.2 Å, its streaking suggests that a random arrangement exists at the level of the asymmetric repeating units, that is, an atactic rather than isotactic structure exists. In the latter case, the relative translation of chains would be well defined in the annealed crystals.

The second layer line corresponds to spacings of approximately 2 Å and shows well-resolved reflections. This observation suggests structural regularity in the backbone atoms and their conformation. Resolution below 4 Å is absent on the equator which is also in line with the atactic hypothesis because isotactic structures usually resolve down to 2 Å or less. Finally, the rather low crystallinity judging from density, line broadening and perfection of X-ray diffraction data also tend to support the atactic structure.

For the 2_1 helical form, first considerations based on chain conformational energy requirements would argue in favor of the crystalline phase containing isotactic block segments. However, examination[10] of the general 2_1 helical conformation, which seems to occur for most α,α'-disubstituted polyesters of the β-propriolactone class, shows that a helix of given handedness is able to accomodate either a D or an L monomer. It seems quite possible that the crystalline structure corresponding to the 2_1 helix of poly(MPPL) is a random copolymer (essentially atactic) with helix handedness showing a statistical vicariance in the crystallite.

Mechanical Properties of MPPL Polyester

The stress-strain curve of MPPL polyester is shown in Figure 5. The curve has the usual characteristics of a semicrystalline polymer with a high initial modulus, a yield point followed by a "neck-in" region, and a stress-hardening region.

In addition, the polymer films exhibit stress softening; that is, the initial modulus decreases after the polymer is prestretched. If left in a relaxed state for several days after stretching, the modulus of the stress-softened film slowly increases again toward its original value. Recovery of the modulus can be hastened by heating the polymer film.

Changes in the crystalline phase of films of MPPL polyester were investigated by wide-angle X-ray diffraction

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(9) G. Natta, *Nuovo Cimento A*, 15 (10), 3 (1960).

(10) J. Cornibert, Ph.D. Thesis, Université de Montréal, 1972.

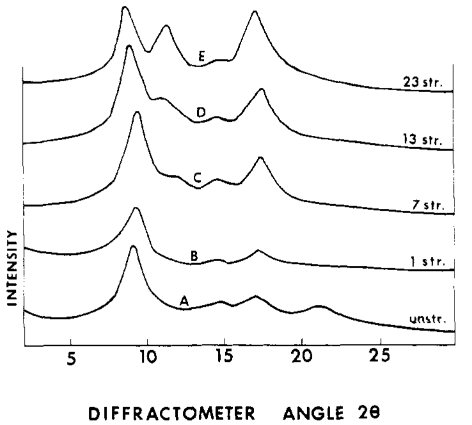

Figure 6. X-Ray diffraction trace: intensity *vs.* scattering angle ($2\theta°$), for PMPPL film which was stretched repeatedly as indicated in the curve labels. The diffractograms correspond to equatorial scans with respect to the direction of stretch.

measurements as a function of elongation. Figure 6 shows these results.

Trace A is that of an unstretched compression-molded film. The peak 2θ values in this trace all correspond to the 2_1 helical conformation.

Trace B is that of the sample after it was stretched once into the reinforcement region of the stress-strain curve. After stretching, the X-ray diffraction trace was recorded in the relaxed state.

After trace B was recorded, the sample was again stretched into the reinforcement region, returned to zero stress and immediately restretched. This procedure was repeated for a total of 5 elongations. Trace C was then recorded.

Traces D and E are the X-ray diffraction traces after similar cycles were run to the total number of elongations indicated.

Table II lists the 2θ values for the diffraction peaks. These peak values are compared with the previously assigned values for both the 2_1 helical and the planar zigzag crystalline forms. The development of a new peak at 2θ = 11.5° and the shift of the 2θ value of the first peak from 9.5 to 8.7° are both attributable to an increase in the amount of the zigzag form, and an apparently concomitant decrease in the helical form. Since the diffractometer traces compare equatorial scans for unstretched and stretched samples and the indexing of the helical reflections is unknown, it is clear that quantitative interpretation of these data should not be attempted. Qualitatively, however, it appears that stretching encourages a helix to zigzag transformation which is reminiscent of the $\alpha \rightarrow \beta$ transformation of keratin due to steam stretching.[11]

Figure 7 shows the stress-strain curves of a film sample of the MPPL polyester that has undergone a cyclic loading program. The sample, 1 in. in length, was first completely necked-in by elongation to 390% and then relaxed at room temperature for 90 minutes. For succeeding cycles a 1-in. specimen was elongated at a rate of 1 in./min to a predetermined strain, immediately returned to zero stress at the same rate, and then allowed to relax at zero stress for 10 min. The curves shown are based upon the dimensions of the sample at the beginning of each cycle.

The increasing self-reinforcement seen with increasing total strain is thought to be a manifestation of permanent orientation, locked-in by formation of the planar zigzag crystalline regions which are generated during the stress cycle. These crystallites are equivalent to a network of physical cross-links, which become the principal load bearer at high extension, but they are metastable and are destroyed by heat-triggered relaxation. It is noteworthy that it takes only a few cycles of strain to establish the initial modulus while the self-reenforcing region shows a constantly increasing modulus at a given strain value. This observation is to be compared with the X-ray data in Table II where the 2θ corresponding to the zigzag form only become prominent after several cycles of stretching.

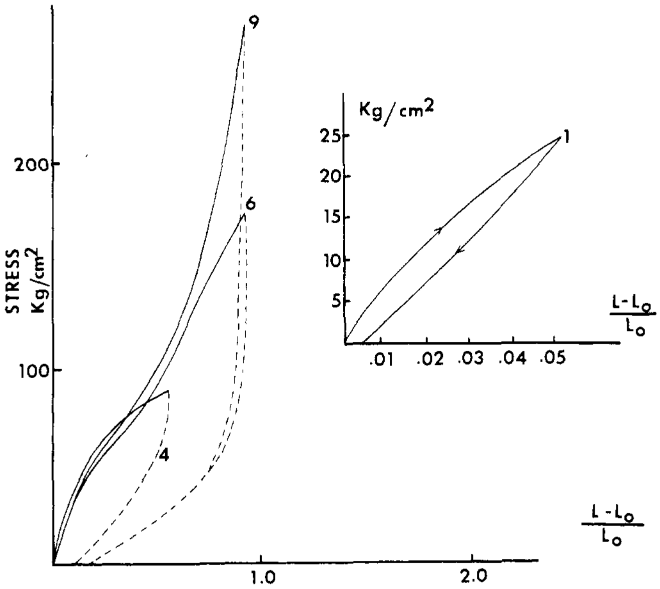

Figure 7. Consecutive, cyclic stress-strain curves for PMPPL. The range of extensions were taken only slightly beyond the Hookean range and illustrate the increased stress hardening with repeated extension.

Thermal Studies

During the thermal analysis of the MPPL polyester by DSC, two melting endotherms were observed. This phenomenon has been observed in other polymers[12-16] and studied extensively, especially for poly(ethylene terephthalate) (PET). Of the two endotherms observed for the MPPL polyester, the one at the higher temperature was usually broad and relatively insensitive to crystallization conditions. In contrast, the lower temperature endotherm occurred with higher crystallization temperatures and longer crystallization times. Increasing the crystallization time increased the relative area of the lower temperature peak. These results are exactly parallel to those found by previous workers for PET.

Recent interpretations[13-15] for PET are that both endothermic peaks represent the melting of folded chain lamellar, and that the temperature at which the lower endotherm occurs is a function of the crystallization conditions. The higher temperature endotherm is believed to be caused by the melting of crystalline regions formed during the DSC temperature program. These crystalline regions can include those that melt during the formation of the lower melting endotherm.

The effect of crystallization temperature on melting for the MPPL polyester is shown in Figure 8. Samples were melted and then quickly quenched to the desired crystal-

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(11) C. H. Bamford, H. Elliott, and W. E. Hanby, "Synthetic Polypeptides," Academic Press, New York, N. Y., 1956.

(12) Z. Pelzbauer and R. St. John Manley, *J. Polym. Sci., Part A2*, 8, 649 (1970).

(13) M. Ikeda, *Kobunsh Kagaku*, 25, 87 (1968).

(14) M. Ikeda, *Kobunsh Kagaku*, 26, 102 (1969).

(15) R. C. Roberts, *J. Polym. Sci., Part B*, 8, 381 (1970).

(16) C. Borri, S. Brückner, V. Crescenzi, G. Della Fortuna, A. Mariano, and P. Bcarazzato, *Eur. Polym. J.*, 7, 1515 (1971).

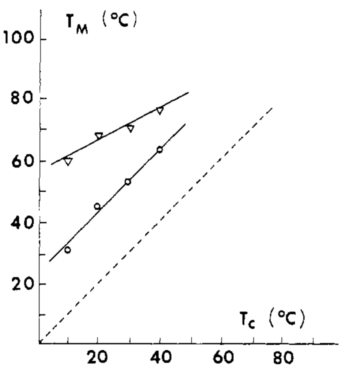

Figure 8. Plot of melting temperature *vs.* temperature of crystallization for PMPPL. The two separate curves correspond to the two endotherms observed. Heating rate was 10°/min.

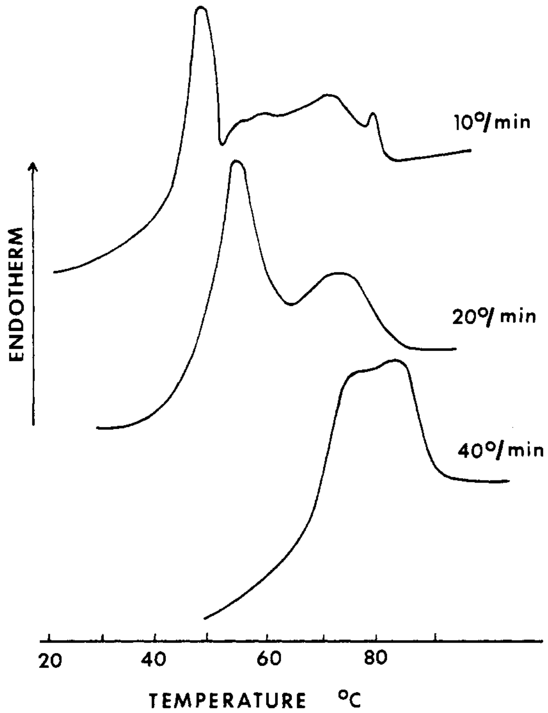

Figure 9. DSC thermograms of PMPPL as a function of heating rate.

lization temperature and crystallized for three hours. Two melting endotherms were observed when the samples were analyzed by DSC. The plots obtained from these analyses are similar to such plots for PET[14] and poly(pivalolactone).[16]

For PET, increasing the rate of heating in the DSC analysis caused the lower temperature endotherm to appear at a higher temperature,[14] and it has been found[15] that for this polymer, the ratio of the area of lower peak to total area increased with increasing heating rate. Figure 9 shows the results of such an experiment with the MPPL polyester. These results are similar to those obtained with PET.

As shown in Figure 10, stretching the MPPL polyester causes a disappearance of the low-temperature endotherm observed on the DSC. The sample used for that analysis was a solvent-cast film that had been dried at 45° crystallized for 3 hr, and then cooled slowly to room temperature. The two melting endotherms are clearly seen. A typical thermogram of such a film after repeated stretching is shown in the lower trace of Figure 10, where it can be seen that the lower temperature peak has disappeared and the high-temperature peak is somewhat broader. Quantitative DSC studies suggested that stretching is accompanied by some loss in crystalline order apparently due to a slippage and unfolding mechanism.[17]

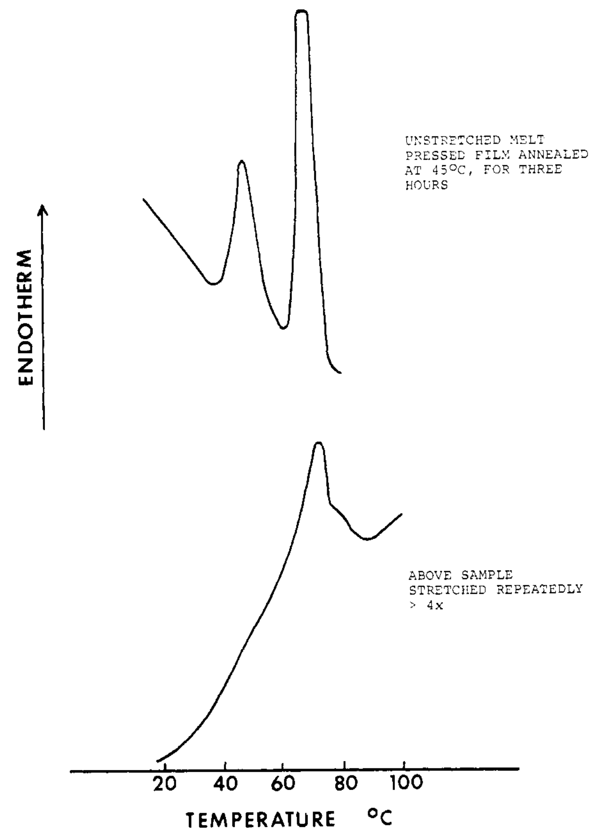

Figure 10. DSC thermogram of annealed, then stretched PMPPL film.

It is tempting to associate the two observed endotherms with the two observed endotherms with the two observed polymorphs: 2_1 helix and planar zigzag forms. However, the similarity of the results with those reported for PET in similar investigations would suggest that the important factor is the existence of differing crystalline perfection in various regions of the sample rather than different polymorphs *per se*. Of course, it is entirely possible that for MPPL polyester crystalline imperfection induced by strain may always imply presence of the zigzag conformation.

Discussion

The presence of crystallinity in nonsymmetrical α,α'-disubstituted polyesters of the MPPL type was reported[2a] previously but no conclusions as to structure were made. It now seems that the X-ray data would argue in favor of an atactic structure or at best a rather low level of stereoregularity which would imply a stereoblock structure. If the crystalline helix of the latter is indeed the same 2_1 helix as found for poly(β-hydroxybutyrate) and poly(pivalolactone), then it is understandable that it may crystallize in spite of a lack of tacticity. Like the Pauling helix for polypeptides, the skeleton or backbone atoms in those two polyesters form the inside of a rather open cylindrical structure while the substituents are pointing to the outside. Molecular models show that it is equally easy to accommodate a D or L monomer in such a helix irrespective of the handedness. However chain packing will clearly be a problem in this case and at best one may expect only paracrystalline order in the 2_1 helical regions.

Another interpretation of the observed crystallinity, is that it corresponds simply to the expected minimum in

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(17) R. J. Samuels in "Plastic Deformation of Polymers," A. Peterlin, Ed., Marcel Dekker Inc., New York, N. Y., 1971.

crystallinity and melting point which is to be expected for an equimolar copolymer from a D,L monomer. This would imply that predominantly D segments of chains segregate from predominantly L segments and form chirally homogeneous crystallites. Since both homopolymers must have the same melting point, a plot of true melting point as a function of antipode composition would show a minimum at the 50 mol % level, *i.e.*, at the composition used in this study. It seems however that in this case, a study of the melting point as a function of comonomer content (*i.e.*, optical purity) would not distinguish between isomorphous substitution or eutectic behavior. In both cases, a minimum at 50 mol % composition is expected.[18] Nevertheless, a knowledge of the complete structure of the optically pure homopolymer would add a great deal to our understanding of how the D,L copolymer crystallizes.

Another possible model is essentially that proposed by Bonart[19] for a poly(ester urethane), which is a copolymer consisting of rigid or "hard" urethane segments and flexible or "soft" polyester segments which alternate regularly ("segmented" polymer). The hard urethane segments are the minor component and were found to separate into discrete domains which showed order in the unstretched state, but upon stretching 200–300%, the beginnings of a new crystalline order was observed. The interpretation of this behavior was that initially on elongation the hard domains rotated in a direction transverse to the direction of elongation while the soft segments oriented and crystallized in the direction of stretch. Upon continued stretching, the hard domains rearranged further until they were sheared into less perfect domains and became oriented in the draw direction.

To apply this interpretation to the polyester of MPPL, the "hard" domains are considered to be the crystallites of the 2_1 helix conformation. During stretching, these crystalline regions never achieve the level of orientation which is characteristic of the crystalline planar zigzag regions. In the process of stretching however the 2_1 helical region eventually become disrupted and the occurrence of both necking-in and stress-softening are taken as indication that this process is occurring.

The corresponding soft phase in this model is then the initial amorphous regions containing exclusively atactic polymer. This phase is readily oriented during stretching and crystallizes in a highly oriented planar zigzag form. Further stretching causes crystalline regions containing the 2_1 helical conformation to be torn apart and further conversion to the zigzag form occurs which, although a crystal of poor order, seems to have a cohesion leading to a higher melting point. Crystallization of the amorphous polymer in this manner would be similar to the stress-induced crystallization of stereoregular elastomers.

The cumulative result of orientation, following these arguments, would be to provide a mechanism for a faster rate of crystallization which is the result seen. Whereas the unstressed MPPL polyester crystallizes slowly at room temperature, over a period of hours, the changes in the physical properties of the polymer during repeated stretching indicate that the crystallization in the oriented state to the panar zigzag form occurs rapidly.

In summary, it is suggested that conditions are available for the stress-induced crystallization of the amorphous regions into the planar zigzag unit cell form in the same manner as for crystallizable elastomers.

Additional support for the proposal that the amorphous chains are able to crystallize in the fully elongated state lies in the simplicity and layered character of the planar zigzag unit cell. The fact that the presumably atactic polymer can crystallize must require that irregularity of side-chain placement will not be a hindrance to crystallization, a mechanism which is operative in the β structure of proteins because of the sheet-like structure.

As noted previously, in the fiber diagram the intensity of diffraction due to the 2_1 helical form increased with time after the stress was removed and the film samples were permitted to relax. This increase is believed to result from recrystallization of the disrupted regions of the helical crystalline form. If the helical form had been transformed completely into the planar zigzag form, this redevelopment of the helical form would not be expected. This same effect was seen in the repeated stretching experiment. The X-ray trace of Figure 6 shows that even after 23 elongations the 2_1 helical form is still seen, as indicated by the 2θ peak at $\sim 14.5°$. This result is probably due in large part to recrystallization at room temperature during the 3 hr it takes to complete an X-ray diffraction trace.

In conclusion, because the atactic polymer can crystallize, the MPPL polyester can be modeled as a domain forming copolymer which can crystallize as two different polymorphs. The stress-strain behavior, including the stress-softening phenomenon, is consistent with this interpretation, although it is not clear whether the domain structure is related to the polymorphism or is purely a morphological phenomenon. Similarly the stress hardening observed after many cycles of stretching is consistent with a domain structure.

Some of the characteristics of this polymer are reminiscent of segmented polyurethanes,[19] others are reminiscent of thermoplastic elastomers. It seems certain that one could achieve a wide range of properties in this one polymer if a selective catalyst were found which allowed development of the desired degree of stereoblock structure.

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