NASA Grant NGR-36-003-054

Part II

INFRARED STUDIES OF THE ORIENTATION PROCESS IN POLYETHYLENE TEREPHTHALATE

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ABSTRACT

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The strain induced crystallinity of stretched polyethylene terephthalate is not temperature dependent below the glass transition temperature, but above it, several crystallization mechanisms are apparently causing temperature dependence.

Sequential biaxial stretching of polyethylene terephthalate films induces more trans content and destroys more gauche content than does simultaneous stretching. The former induces a slight orientation in the transverse direction; the latter produces no orientation. Neither process is molecular weight or draw rate dependent.

Cyclic mechanical and thermal treatments show that annealing drawn samples further increases trans content and produces chain folding. Redrawing destroys folding, but increases trans content. Reannealing reproduces folding without increasing trans structure.

INTRODUCTION

A theory for obtaining three dimensional infrared measurements by performing tilting experiments in oriented polymers systems has been proposed.(1) Previous investigators reported results for polyethylene terephthalate in terms of directional absorbances(1,2) and also in terms of a reduced structure factor as a function of both density and draw ratio. Plots of A_o' (973) vs density reveal that the induced trans content exists in the amorphous regions of the film, while plots of A_o' (973) vs draw ratio indicate that the amount of induced trans structure increases linearly with a draw ratio.

In this paper orientation will be reported in terms of a dichroic ratio: $Ryx = A_y/A_x = A_{11}/A_{\perp}$. The change in structure will be presented in terms of a change in reduced structure factor value. This quantity is used instead of the directional absorbance because 1) it is less subject to error fluctuation, and 2) the amount of induced structure is of greater interest than is the directional orientation, which may have dubious meaning because of the relatively high error associated with it. The change in reduced structure factor is the value for the stretched film less the value for the unstretched film. The structure factor is defined as: $A_o = (A_x + A_y + A_z)/3$, and the reduced structure factor by: $A_o' = A_o\ (band)/A_o(ITB)$. Dividing by the internal thickness band places all the measurements on a common thickness basis. The subscripts refer to the film coordinates; y is the stretch direction, x is the transverse direction, and z is the thickness direction. These results will be presented as a function of draw temperature for uniaxial drawing and as a function of draw rate for biaxial drawing.

A detailed explanation of the tilting technique and the calculational procedure has been reported.(3) Also, a detailed consideration of the corrections necessary to compensate for errors in the measuring procedure was proported. This analysis includes the effects of 1) machine polarization, 2) polarizer inefficiency, 3) sample birefringence, 4) anisotropy of the index of refraction, and 5) anisotropy of scattering from the film surface. The latter three effects were also studied for polyethylene terephthalate and the necessary corrections employed.

A. Experimental

Amorphous solution cast films of polyethylene terephthalate were obtained from DuPont* These samples had an intrinsic viscosity range of 0.54-0.56 in tetrachloroethylene-phenol solution, and a number averaged molecular weight as determined by end group analysis of about 15,000. These samples had essentially zero crystallinity as determined by x-ray scattering.(4)

A specimen of the 2.4 mil. film was cold drawn in the hand stretcher to 450% elongation and then heat set while in tension at 200°C for 10 hours. A second such specimen was cold drawn in the hand stretcher to 430% elongation, annealed in tension at 140°C for 30 minutes, redrawn in the Instron at 0.1 in./min. at 65°C to an additional 50% elongation, making the total elongation 645%. This sample was placed in tension hand tight and annealed at 140°C for 30 minutes. A specimen of the 0.8 mil. amorphous cast film was heat set at 240°C for 5 min. These samples were used to determine the effect of heat and strain induced crystallization in polyethylene terephthalate films.

Specimens of the 0.8 mil. film were used as the undrawn samples. Strips of the 2.4 mil. film were uniaxially drawn, employing both a hand stretching device and also the Instron with oven enclosure, to less than 1 mil. thickness. The samples drawn in the Instron below the glass transition temperature were drawn at 0.2 in./

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*C.J. Heffelfinger, Circleville Laboratories, E.I. duPont de Nemours & Co., Inc.

min. to approximately 480% elongation. Those drawn above the glass transition temperature were drawn at 20.0 in./min. to approximately 550% elongation. The latter samples were held in tension until the oven cooled to 50°C or lower before the jaws were released. Some undrawn specimens were heated in the Instron oven at the different drawing temperatures above the glass transition for 10 minutes.

Prior to drawing, the specimens of polyethylene terephthalate were marked with an ink grid from a rubber stamp. These marks were used after drawing to determine the draw ratio. A portion in the center of the uniaxially drawn film was used as the sample.

Two different molecular weight films of polyethylene terephthalate were biaxially oriented in a T.M. Long Stretcher. The use of the stretcher was supplied by NASA*. The high molecular weight material has a number averaged molecular weight of 18,900 based on an intrinsic viscosity of 0.67. The lower molecular weight material has a number averaged molecular weight of 13,800 based on an intrinsic viscosity of 0.52. These viscosities were measured using a solution of 60-40% trichloroethylene and phenol as solvent at 30°C.(5)

The biaxially oriented films were drawn using rates of 2.5, 6.0, 10.1, and 22.5 in./sec. at 85°C to a 300% elongation. The biaxial orientation was accomplished by simultaneous stretching in the machine and transverse directions and also by sequential stretch-

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ing, first in the machine direction and then in the transverse direction.

B. Sample Examination

The thin film samples of polyethylene terephthalate described in the preceding section were examined using a Perkin-Elmer 521 Grating Infrared Spectrophotometer. Two six plate Perkin-Elmer silver chloride polarizers were mounted at 45° to the photometer entrance in both sample and reference beams. A variable angle tilting mechanism, mounted between the polarizer and the photometer entrance in the sample beam, was employed to tilt the films at the necessary angles for the calculations. The angles, 0° and 42° were used, the latter value was the upper limit of the available angles, due to space limitations. Eight infrared measurements per film were required. The analysis of these measurements and the necessary corrections are described in a previous paper.(3)

C. Results

1. Effect of Draw Temperature on Uniaxial Orientation

Orientation and structure factor values for undrawn amorphous polyethylene terephthalate are tabulated in Table I. For the temperatures above the glass transition temperature, amorphous film samples were subjected to the thermal film drawing treatment for ten minutes to determine if heat induced crystallization would occur.

After the treatment the films were randomly oriented and did not show any evidence of crystallization. The experimental times appear to be shorter than the nucleation induction times. The film treated at 120°C has A'_o values which are slightly higher than the values at the other temperatures. The $\Delta A'_o$ values for the drawn films above the glass transition temperature were calculated using the individual A'_o values for the undrawn samples at the draw temperature. All others were computed using the average A'_o values for the five room temperature undrawn samples.

Samples of amorphous cast film were uniaxially drawn, both below and above the glass transition temperature, at constant rate and nearly constant elongation. Figures 1 and 2 show the change in A'_o values for these different stretchings as a function of temperature. Below the glass transition temperature (Table II), the slight orientation observed does not appear to be a function of temperature. Similarly to polyethylene,(3) the crystalline regions orient to a higher degree than the amorphous regions, but the induced orientation is not as pronounced. Trans content is induced by stretching at the expense of gauche content. The decrease in gauche content is the same for all temperatures, except just below the glass transition temperature, where a greater loss occurs. The induced trans content is not a function of temperature for the lower temperatures, but near the glass transition temperature the induced crystalline content decreases. This decrease is probably due to a decrease in the severity of the deformation process, since as the transition temperature is approached, and the chains become more mobile. In the main, the induced structure below the glass transition temperature is not a function of temperature.

Above the glass transition temperature, drawing is much easier than at room temperature. In fact, draw rates of 20.0 in./min. or higher are necessary to form a neck, in comparison with 0.2 in./min. required below the glass transition. As the draw temperature approaches annealing temperatures, the increased chain mobility should cause a decrease in the severity of the deformation process. At the 20.0 in./min. draw rate, a decrease in deformation severity with increasing temperature was experimentally observed. The sample at 85°C deformed by erratic necking; at 90°C it deformed by uniform necking, followed by uniform stretching after the neck was formed; and at 95°C and higher temperatures, deformation occurred by uniform stretching. As the temperature increased, the stretching became more fluid-like.

The A'_o values are not a simple function of temperature, as is shown in Figure 1 and 2. After an initial increase in trans content at 85°C, samples stretched at successively higher temperatures exhibit a relative decline in the amount of induced trans structure, corresponding to the decreasing severity of the drawing process. The induced trans content does not continue to decline to a lower value at 120°C, but rises sharply at 105°C and continues to rise at 120°C. This unanticipated rise in trans content at 105°C is due to the onset of heat induced crystallization. In undrawn films the crystallization half times (6) decreases as the temperature increases. However, the induction times for the undrawn films are sufficient that no crystallization effects at 105°C are noticed for the heat treatment of ten minutes. The deformation process depresses the nucleation induction time by providing nucleation sites on the deformed material. Thus, heat induced crystallization occurring in stretched films at 105°C is within the experimental time scale. Although the strain induced crystallinity at 120°C may be decreasing, the heat induced crystallinity is increasing, causing a net rise in crystallinity at 120°C. The change in gauche content upon drawing decreases from the value at 85°C with increasing temperature. This result is contrary to intuition, which would predict a relative gauche content increase with temperature up to 105°C to correspond with the observed relative decrease in trans content. Increased molecular motion with increasing temperature could cause a greater destruction of gauche isomer. Because of its crystalline nature, the trans isomer is more immune to this kind of thermal destruction. Again at 105°C a sharp rise in gauche content is noticed, due in part to newly formed gauche folded structure, but due primarily to a different time scale effect. Annealing experiments (7) which measured absorbance as a function of time revealed an initial increase in the gauche content before a decrease arising from heating induced crystallization conversion of gauche into trans. The time scale at the gauche peak corresponds to the time scale of the stretching experiments. In this light it appears that while stretching depresses the crystallization induction times, stretching does not influence gauche time effects, since the gauche structure behaves as it does for undrawn heat treated samples and depends only on temperature. At 120°C the gauche content is lower, indicating the temperature dependent transient effects no longer appear. The gauche content at 120°C is slightly lower than 85°C, corresponding to a slightly higher trans content than at 85°C.

Examination of the orientation parameter for drawing above the glass transition temperature (Table III) reveals a slight decrease in R_{yx} values with temperature up to 105°C. This corresponds with the observed decrease in deformation severity. However, the crystalline region orientation increases at 105°C and also at 120°C. This increase corresponds to the heat induced crystallinity contribution. Thus, while heat induced crystallization alone does not affect the orientation of the crystallites, heat induced crystallization during deformation aligns the crystallites more highly with the draw direction than is observed for only strain induced crystallization.

In conclusion, the results for uniaxial drawing above the glass transition temperature indicate several mechanisms at work during the crystallization process. The inter-relationship of these mechanisms is extremely complicated, but it is apparent that they include:

1) severity of deformation process,
2) effect of deformation and temperature on nucleation and crystallization times, and

3) thermal molecular motion.

At present no quantitative analysis of these mechanisms can be constructed.

2. Effect of Draw Rate on Biaxial Orientation

Samples of amorphous cast film were biaxially oriented on a T. M. Long Stretcher at 85°C to a 300% elongation. Two identical amorphous samples were drawn at a given rate; one was sequentially drawn, first in the machine direction and then in the transverse direction, and the other was simultaneously drawn. The difference in induced structure based on an undrawn sample given the same thermal treatment at 85°C is shown in Figures 3-6. Both high and low molecular weight films were used in the biaxial orientation experiments and are reported in Tables IV and V, respectively. No specimens of these films 1.0 mil. thick were available as undrawn samples. An undrawn moderate molecular weight sample used for the uniaxial orientation work was used as the undrawn sample. Consequently, the $\Delta A_o'$ values reported here are not accurate on an absolute basis, and no comparison between the high and the low molecular weight materials for a given draw rate can be made. However, comparisons for the same molecular weight material at different draw rates are valid.

The dichroic ratios in Tables IV and V show no specific orientation of the crystalline or amorphous regions for simultaneously stretching, since the force was the same in both machine and transverse directions. But sequentially drawn samples were drawn at constant rate, rather than at constant force, so there should be a slight preferential orientation in the transverse direction due to the larger strain in that direction. This is exactly what is observed in Tables IV and V for the 6.0 and 10.1 in./sec. draw rates for both molecular weight samples, and for the 2.5 and 22.5 in./sec. draw rates for the low molecular weight samples. The high molecular weight results are inconsistent with the other results. Sequential drawing at constant force should produce random orientation.

Structure factor values and change in structure factor values are also reported in Tables IV and V. The $\Delta A_o'$ values are shown graphically in Figures 3-6. In all cases the draw rate does not determine the amount of structure induced by either the simultaneous or the sequential stretching process for the very fast draw rates obtained on the T. M. Long Stretcher. Sequential stretching of high molecular weight material destroys more gauche isomer than does simultaneous stretching, but the induced trans content is only slightly higher.

For the low molecular weight material, sequential stretching destroys more amorphous structure than does simultaneous stretching, and induces more crystalline structure based on the 973 cm^{-1} band. The 973 cm^{-1} band is used here instead of the 848 cm^{-1} band to characterize the crystalline areas because of the extreme thinness of the low molecular weight samples.

In conclusion, sequential stretching destroys more amorphous content and induces slightly more crystalline content for both high and low molecular weight films than does simultaneous stretching. There is not an appreciable rate dependence associated with this process. Sequential stretching causes a slightly preferential orientation in the transverse direction; simultaneous stretching causes no preferential orientation.

3. Effect of Strain and Heat on Crystallinity

Commerical production of polyethylene terephthalate films utilizes both strain and heat induced crystallization to produce films with more impact strength and dimensional stability. When a glassy film is first stretched and then heat set, it exhibits a higher trans content than a film which has undergone either of these two treatments separately. Commerical film production usually involves two-way stretching followed by heat setting. Other variations, notably post-stretching the biaxially oriented film after heat setting, have been reported.(2)

The spectra of an amorphous undrawn film, a stretched film, and a heat set stretched film are shown in Figure 7. The intensities of the analytical bands show graphically the change in isomeric structure due to these treatments. In Table VI, A are reported R_{yx}, A'_o, and $\Delta A'_o$ values for a heat set glassy film, a stretched glassy film, and a heat set stretched film. These treatments cause an increase in the trans content at the expense of the gauche content.

The orientation induced by drawing relaxes upon annealing, but does not revert completely to the random orientation exhibited in the amorphous film.

The effect of a series of uniaxial stretching and annealing processes on the crystallinity of a polyethylene terephthalate was examined. From prior knowledge, an initial draw ratio of about 400% induces crystalline structure, but retains enough gauche structure so the film can be further drawn. An annealing temperature of 140°C imparts crystalline structure, but does not make the unoriented film brittle, as higher temperatures tend to do. There is little temperature dependence on A_o below the glass transition temperature, so a drawing temperature of 65°C will have the same effect of crystallinity as drawing at 25°C, but drawing at 65°C does not fracture the film.

An amorphous cast film was cold drawn at room temperature to 430% elongation, annealed at 14°C for 30 minutes, redrawn in the same direction an additional 50% (645% total) elongation at 65°C, and finally reannealed at 140°C for 30 minutes. The results for this series of mechanical and thermal treatments are shown in Table XVIB. The cold drawn sample exhibits a higher trans content at the epense of the gauche content. Annealing the stretched film further increases the crystallinity. However, there is a relative increase in gauche content due to the occurrence of chain folding which is exhibited by the appearance of the 988 cm^{-1} band. A second stretching destroys the chain folding, reduces the gauche content to the level it was prior to annealing, and slightly increases the crystalline content. A second annealing does not appear to change the crystallinity appreciably, but does restore the folded structure. Along with this folding is a relative increase in gauche content.

An analysis of the orientation changes occurring during this cycle of mechanical and thermal treatments reveals an initial orientation of the crystalline regions with the first stretching. Annealing relaxes the uniaxial orientation toward a random orientation. The second stretching is not severe enough to induce further orientation. The second annealing further relaxes the orientation.

The 988 cm^{-1} band has been systematically examined and assigned to a folded structure in polyethylene terephthalate.(8) This band appears during heat induced crystallization at lower temperatures. Strain and heat induced crystallization occur simultaneously if the drawing temperature is high enough. The 988 cm^{-1} fold band is observed in the samples drawn at 105°C and higher temperatures.

CONCLUSIONS

Both stretching and heat setting amorphous polyethylene terephthalate impart crystalline structure to the amorphous films. Heat setting a stretched film induces more trans structure than is achieved by the individual treatments. Orientation induced by drawing relaxes upon heat setting. Annealing stretched films continues to increase the trans content induced by drawing, increases the gauche content due to chain folding, and relaxes the stretched induced orientation. A second stretching further increases the trans content and destroys folded regions, thus lowering the gauche content. A second annealing reforms folded structure, but does not increase the trans content appreciably; strain induced orientation relaxes further.

During uniaxial stretching of polyethylene terephthalate below the glass transition temperature, the amount of induced trans structure at the expense of gauche structure is nearly constant and is not a function of temperature. Crystalline regions orient upon drawing, but not to the extent exhibited by polyethylene crystallites. Uniaxial drawing above the glass transition temperature depends on several crystallization mechanisms as a function of temperature. Effects contributing to crystallization in this region are:

1) severity of the deformation process,
2) effect of both deformation and temperature on nucleation and crystallization times, and

3) thermal molecular motion.

Simultaneous biaxial stretching at constant draw rate in both directions does not induce any orientation, while sequential biaxial stretching induces a slight preferential orientation in the transverse direction. Sequential biaxial stretching induces slightly more trans content and destroys more gauche content than does simultaneous biaxial stretching for both high and low molecular weight films. The amount of induced structure for both processes is not appreciably dependent on draw rate at these fast draw rates.

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Table I

UNSTRETCHED POLYETHYLENE TEREPHTHALATE

		Amorphous						Crystalline					
		896 cm^{-1}			1042 cm^{-1}			848 cm^{-1}			973 cm^{-1}		
Temp.	Elong	R_{yx}	A'_o	$\Delta A'_o$	R_{yx}	A'_o	$\Delta A'_o$	R_{yx}	A'_o	$\Delta A'_o$	R_{yx}	A'_o	$\Delta A'_o$
25	0	0.99	1.40	0	0.97	2.36	0	0.95	0.81	0	0.90	0.34	0
		1.07	1.36		1.08	2.17		1.13	----		1.03	0.32	
		1.04	1.36		0.98	2.13		1.02	0.87		1.04	0.27	
		1.08	1.34		1.12	2.08		1.06	0.87		1.28	0.27	
		0.86	1.20		0.85	----		0.85	0.83		0.88	0.26	
AVG			1.33			2.19			0.85			0.29	
85		0.98	1.28		1.00	2.18		0.95	0.70		0.88	0.29	
90		1.00	1.42		1.00	2.18		1.00	0.91		1.00	0.38	
95		1.01	1.30		0.98	2.16		1.03	0.74		1.06	0.29	
100		1.00	1.39		1.00	2.26		1.00	1.17		----	0.52	
105		1.01	1.33		1.00	2.04		1.01	0.87		1.04	0.37	
120		1.03	1.72		0.97	2.52		1.09	0.97		----	0.42	

Table II

UNIAXIALLY STRETCHED POLYETHYLENE TEREPHTHALATE BELOW GLASS TRANSITION

		Amorphous						Crystalline					
		896 cm^{-1}			1042 cm^{-1}			848 cm^{-1}			973 cm^{-1}		
Temp	Elong	R_{yx}	A'_o	$\Delta A'_o$	R_{yx}	A'_o	$\Delta A'_o$	R_{yx}	A'_o	$\Delta A'_o$	R_{yx}	A'_o	$\Delta A'_o$
25	430	0.90	0.79	-0.54	1.16	1.00	-1.19	1.47	1.39	+0.54	5.9	1.55	+1.26
25	430	0.82	0.89	-0.44	1.11	0.76	-1.43	1.29	1.47	+0.62	7.1	1.53	+1.24
25	450	0.97	0.91	-0.42	1.33	0.96	-1.23	1.85	1.51	+0.66	7.0	1.72	+1.43
25	460	0.87	0.77	-0.56	1.12	0.63	-1.56	1.35	1.65	+0.80	7.6	1.86	+1.57
25	460	0.84	0.75	-0.58	0.66	0.72	-1.47	1.30	1.65	+0.80	8.2	1.85	+1.56
25	470	1.09	0.79	-0.54	0.86	0.54	-1.65	1.56	1.57	+0.72	5.2	1.82	+1.53
25	470	1.07	0.78	-0.55	0.88	0.69	-1.50	1.60	1.61	+0.76	6.6	1.78	+1.49
25	500	1.18	0.75	-0.58	1.13	0.83	-1.36	1.71	1.52	+0.67	7.6	1.51	+1.22
45	480	0.95	0.80	-0.47	0.98	0.82	-1.39	1.53	1.66	+0.71	7.5	1.91	+1.46
45	480	0.69	0.86	-0.53	1.21	0.80	-1.37	1.62	1.56	+0.81	7.7	1.75	+1.62
65	440	0.92	0.66	-0.67	1.15	0.94	-1.25	1.32	1.40	+0.55	6.4	1.34	+1.05
65	480	1.12	0.73	-0.60	1.26	0.69	-1.50	1.46	1.48	+0.63	6.4	1.29	+1.00

Table III

UNIAXIALLY STRETCHED POLYETHYLENE TEREPHTHALATE ABOVE GLASS TRANSITION

		Amorphous						Crystalline					
		$896\ cm^{-1}$			$1042\ cm^{-1}$			$848\ cm^{-1}$			$973\ cm^{-1}$		
Temp.	Elong.	R_{yx}	A_o'	$\Delta A_o'$	R_{yx}	A_o'	$\Delta A_o'$	R_{yx}	A_o'	$\Delta A_o'$	R_{yx}	A_o'	$\Delta A_o'$
85	460	0.96	1.32	----	1.06	1.55	-0.63	1.53	1.67	+0.97	5.6	2.08	+1.79
85	500	0.82	0.90	-0.38	1.23	1.30	-0.88	1.27	2.03	+1.33	5.8	2.19	+1.90
95	530	0.88	0.74	-0.56	1.18	0.97	-1.19	1.28	1.67	+0.93	5.5	1.59	+1.30
100	560	0.76	0.71	-0.68	0.94	0.75	-1.51	1.17	1.90	+0.73	5.2	1.97	+1.45
105	560	1.14	1.11	-0.22	0.97	1.32	-0.72	1.67	2.07	+1.20	7.7	2.09	+1.72
120	700	1.12	1.08	-0.68	1.16	1.53	-1.01	1.55	2.26	+1.25	6.7	2.34	+1.88

Table IV

BIAXIALLY STRETCHED POLYETHYLENE TEREPHTHALATE
HIGH MOLECULAR WEIGHT

		Amorphous						Crystalline					
		896 cm^{-1}			1042 cm^{-1}			848 cm^{-1}			973 cm^{-1}		
Type	Rate	R_{yx}	A'_o	$\Delta A'_o$	R_{yx}	A'_o	$\Delta A'_o$	R_{yx}	A'_o	$\Delta A'_o$	R_{yx}	A'_o	$\Delta A'_o$
SIM	2.5	1.05	1.24	-0.29	0.95	2.05	-0.77	1.16	1.64	+0.83	1.05	1.53	+1.16
SIM	2.5	1.05	0.91	-0.62	1.05	1.61	-0.33	1.00	1.49	+0.68	0.91	1.37	+1.00
SIM	6.0	1.01	1.23	-0.30	1.05	1.56	-0.82	1.01	1.51	+0.70	1.02	1.44	+1.07
SIM	10.1	1.04	1.11	-0.042	0.99	1.53	-0.85	1.04	1.28	+0.47	1.00	1.34	+0.97
SIM	10.1	1.10	1.13	-0.40	1.01	1.58	-0.80	1.07	1.33	+0.52	1.00	1.43	+1.06
SIM	22.5	1.02	1.15	-0.38	0.98	1.65	-0.73	1.04	1.56	+0.75	1.01	1.37	+1.00
SEQ	2.5	1.52	1.07	-0.46	0.88	1.32	-1.06	1.24	1.94	+1.13	0.72	1.63	+1.26
SEQ	2.5	1.26	0.93	-0.60	1.17	1.35	-1.03	1.04	1.54	+0.73	0.80	1.67	+1.30
SEQ	6.0	0.83	0.67	-0.84	0.86	0.85	-1.53	0.80	1.29	+0.48	0.67	1.38	+1.01
SEQ	6.0	0.60	0.89	-0.64	0.81	1.09	-1.29	0.84	1.52	+0.71	0.71	1.71	+1.34
SEQ	10.1	0.72	0.94	-0.59	1.01	1.05	-1.33	0.84	1.44	+0.63	0.65	1.48	+1.11
SEQ	10.1	0.70	0.97	-0.56	1.04	1.10	-1.28	0.82	1.43	+0.62	0.68	1.47	+1.10
SEQ	22.5	1.33	0.80	-0.73	1.05	0.93	-1.45	1.38	1.48	+0.67	1.79	1.50	+1.13
Undrawn		0.98	1.53	0	0.97	2.38	0	1.01	0.81	0	1.02	0.37	0

Table V

BIAXIALLY STRETCHED POLYETHYLENE TEREPHTHALATE LOW MOLECULAR WEIGHT

		Amorphous						Crystalline					
		896 cm^{-1}			1042 cm^{-1}			848 cm^{-1}			973 cm^{-1}		
Type	Rate	R_{yx}	A'_o	$\Delta A'_o$	R_{yx}	A'_o	$\Delta A'_o$	R_{yx}	A'_o	$\Delta A'_o$	R_{yx}	A'_o	$\Delta A'_o$
SIM	2.5	0.92	1.18	-0.35	0.90	1.70	-0.68	1.26	1.40	+0.59	1.59	1.25	+0.88
SIM	6.0	1.03	0.99	-0.54	1.00	1.75	-0.63	0.81	1.30	+0.49	0.70	1.56	+1.19
SIM	6.0	1.01	1.08	-0.45	1.00	2.00	-0.38	0.81	1.48	+0.67	0.75	1.76	+1.39
SIM	6.0	1.00	0.86	-0.67	0.96	1.22	-1.16	1.00	1.32	+0.51	0.94	1.18	+0.81
SIM	10.1	2.70	1.13	-0.40	0.45	1.03	-1.35	2.12	1.45	+0.64	0.55	1.04	+0.67
SIM	10.1	0.92	1.04	-0.49	1.03	1.52	-0.86	1.18	1.27	+0.46	1.41	1.13	+0.76
SIM	22.5	1.02	1.16	-0.37	0.93	1.38	-1.00	1.12	1.52	+0.71	0.97	1.28	+0.91
SEQ	2.5	1.20	0.79	-0.74	0.76	0.94	-1.44	0.92	1.36	+0.55	0.44	1.33	+0.96
SEQ	6.0	1.18	0.84	-0.69	0.79	1.08	-1.30	0.83	1.77	+0.96	0.41	1.83	+1.46
SEQ	6.0	1.01	1.15	-0.38	0.77	1.41	-0.97	0.89	2.24	+1.53	0.46	2.38	+2.01
SEQ	10.1	0.88	0.81	-0.72	1.06	1.37	-1.01	0.81	1.28	+0.47	0.67	1.54	+1.17
SEQ	10.1	0.64	1.00	-0.53	1.09	1.33	-1.05	0.71	1.32	+0.51	0.61	1.65	+1.28
SEQ	22.5	1.14	1.00	-0.53	0.60	0.88	-1.50	1.21	1.95	+1.14	1.92	1.82	+1.45
SEQ	22.5	1.00	0.91	-0.62	1.50	----	-----	0.84	1.82	+1.01	0.48	1.63	+1.26
Undrawn		0.98	1.53	0	0.97	2.38	0	1.01	0.81	0	1.02	0.37	0

Table VI

UNIAXIALLY STRETCHED POLYETHYLENE TEREPHTHALATE STRAIN AND HEAT INDUCED CRYSTALLIZATION

		Amorphous						Crystalline								
		896 cm^{-1}			1042 cm^{-1}			988 cm^{-1}			848 cm^{-1}			973 cm^{-1}		
Temp	Elong	R_{yx}	A'_o	$\Delta A'_o$	R_{yx}	A'_o	$\Delta A'_o$	R_{yx}	A'_o	$\Delta A'_o$	R_{yx}	A'_o	$\Delta A'_o$	R_{yx}	A'_o	$\Delta A'_o$
A. Strain and Heat Set																
240	0	1.00	0.83	-0.50	1.03	1.36	-0.83	0.98	0.30	+0.30	0.99	1.69	+0.84	0.99	1.76	+1.47
25	450	0.97	0.91	-0.42	1.33	0.96	-1.23	----	0	0	1.85	1.51	+0.66	7.0	1.72	+1.43
200	450	0.97	0.76	-0.57	1.15	0.91	-1.28	----	----	-----	0.96	2.54	+1.69	3.4	2.83	+2.54
B. Strain and Annealed																
25	430	0.82	0.89	-0.44	1.11	0.76	-1.43	----	0	0	1.29	1.47	+0.62	7.1	1.53	+1.24
140	430	0.96	0.96	-0.37	1.16	1.10	-1.09	2.90	0.35	+0.35	1.45	2.10	+1.25	4.7	1.94	+1.65
65	645	1.24	0.70	-0.63	0.89	0.74	-1.45	----	0	0	1.08	2.13	+1.28	4.3	2.03	+1.74
140	645	0.98	0.84	-0.49	1.11	0.93	-1.22	2.11	0.35	+0.35	0.99	2.19	+1.34	3.8	1.99	+1.70

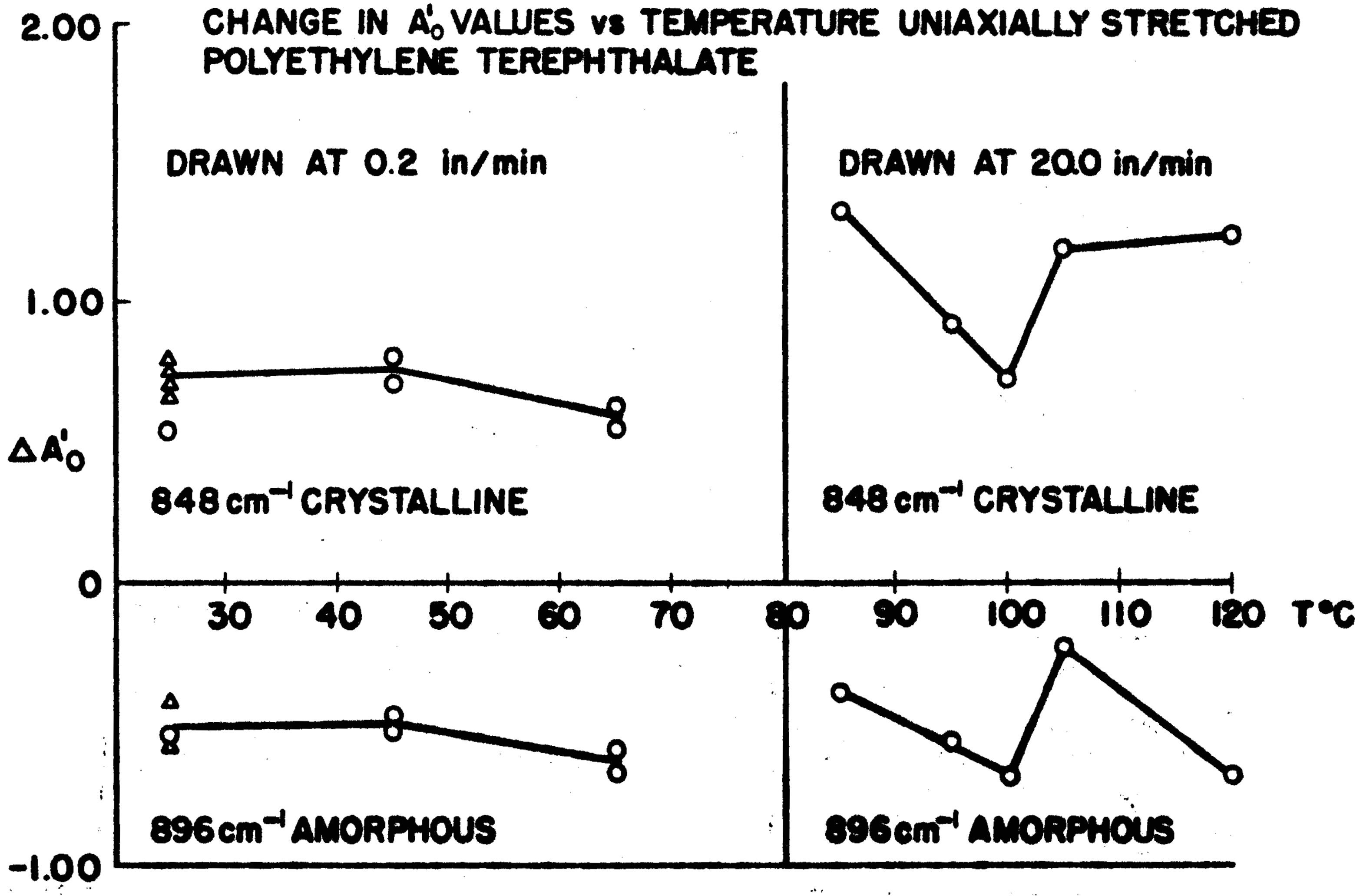
CHANGE IN A'_0 VALUES vs TEMPERATURE UNIAXIALLY STRETCHED POLYETHYLENE TEREPHTHALATE
DRAWN AT 0.2 in/min
DRAWN AT 20.0 in/min
848 cm^{-1} CRYSTALLINE
848 cm^{-1} CRYSTALLINE
896 cm^{-1} AMORPHOUS
896 cm^{-1} AMORPHOUS
2.00
1.00
$\Delta A'_0$
0
-1.00
30
40
50
60
70
80
90
100
110
120
T°C

Figure 1

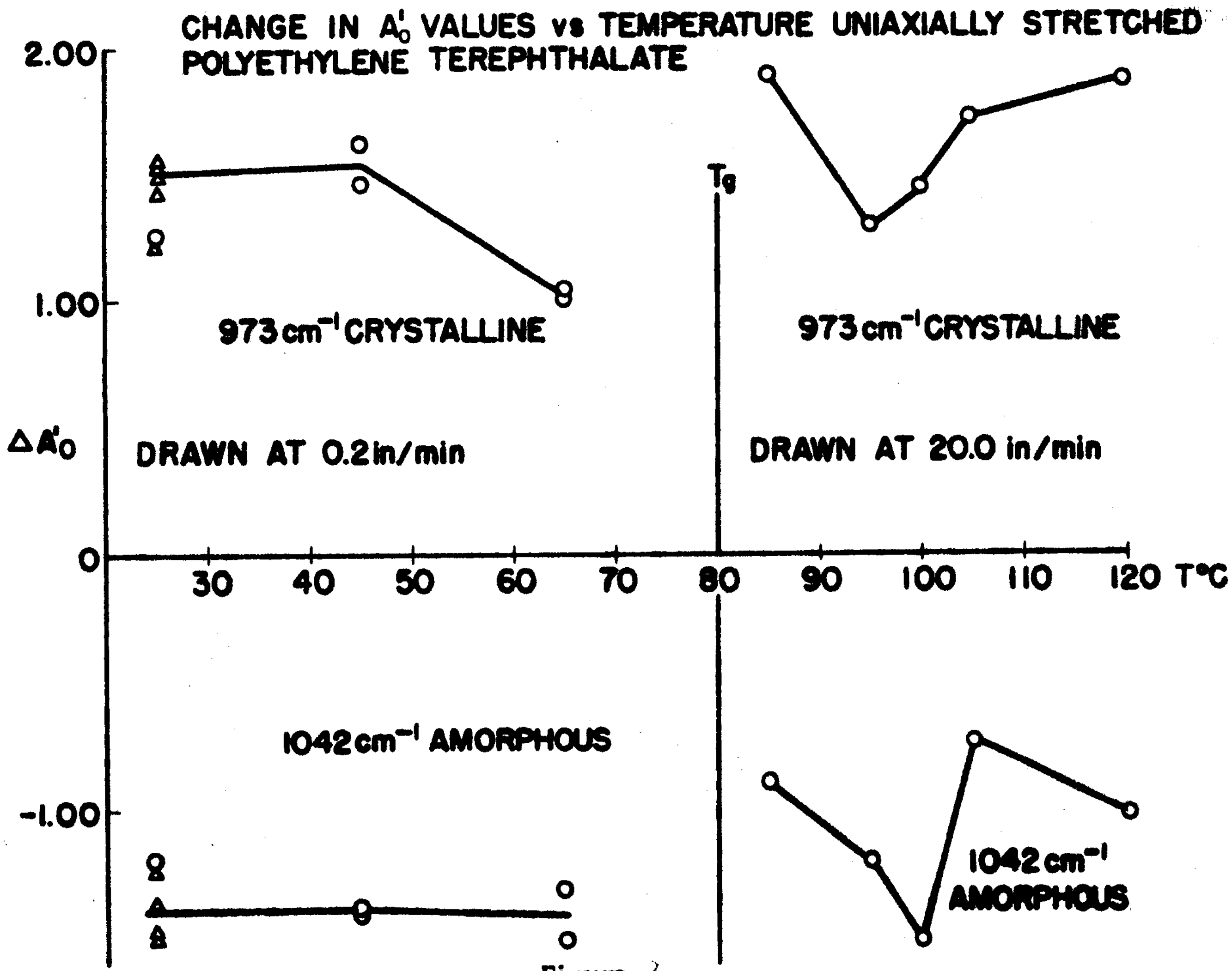
CHANGE IN A'₀ VALUES vs TEMPERATURE UNIAXIALLY STRETCHED POLYETHYLENE TEREPHTHALATE
2.00
1.00
0
-1.00
ΔA'₀
30
40
50
60
70
80
90
100
110
120 T°C
Tg
973 cm⁻¹ CRYSTALLINE
DRAWN AT 0.2 in/min
1042 cm⁻¹ AMORPHOUS
973 cm⁻¹ CRYSTALLINE
DRAWN AT 20.0 in/min
1042 cm⁻¹ AMORPHOUS

Figure 2.

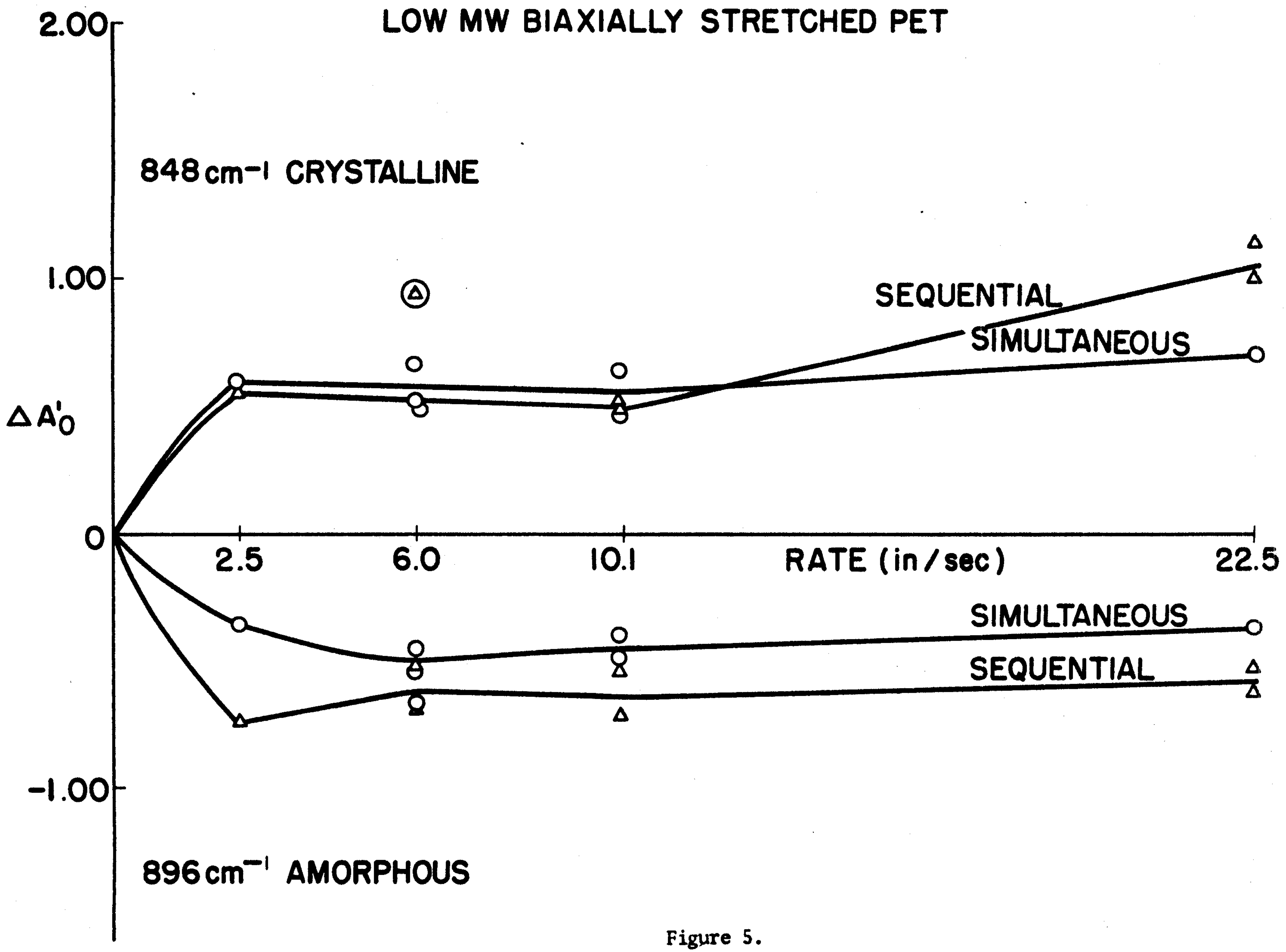
LOW MW BIAXIALLY STRETCHED PET
2.00
1.00
0
-1.00
$\Delta A'_0$
848 cm^{-1} CRYSTALLINE
896 cm^{-1} AMORPHOUS
SEQUENTIAL
SIMULTANEOUS
2.5
6.0
10.1
RATE (in / sec)
22.5
SIMULTANEOUS
SEQUENTIAL

Figure 5.

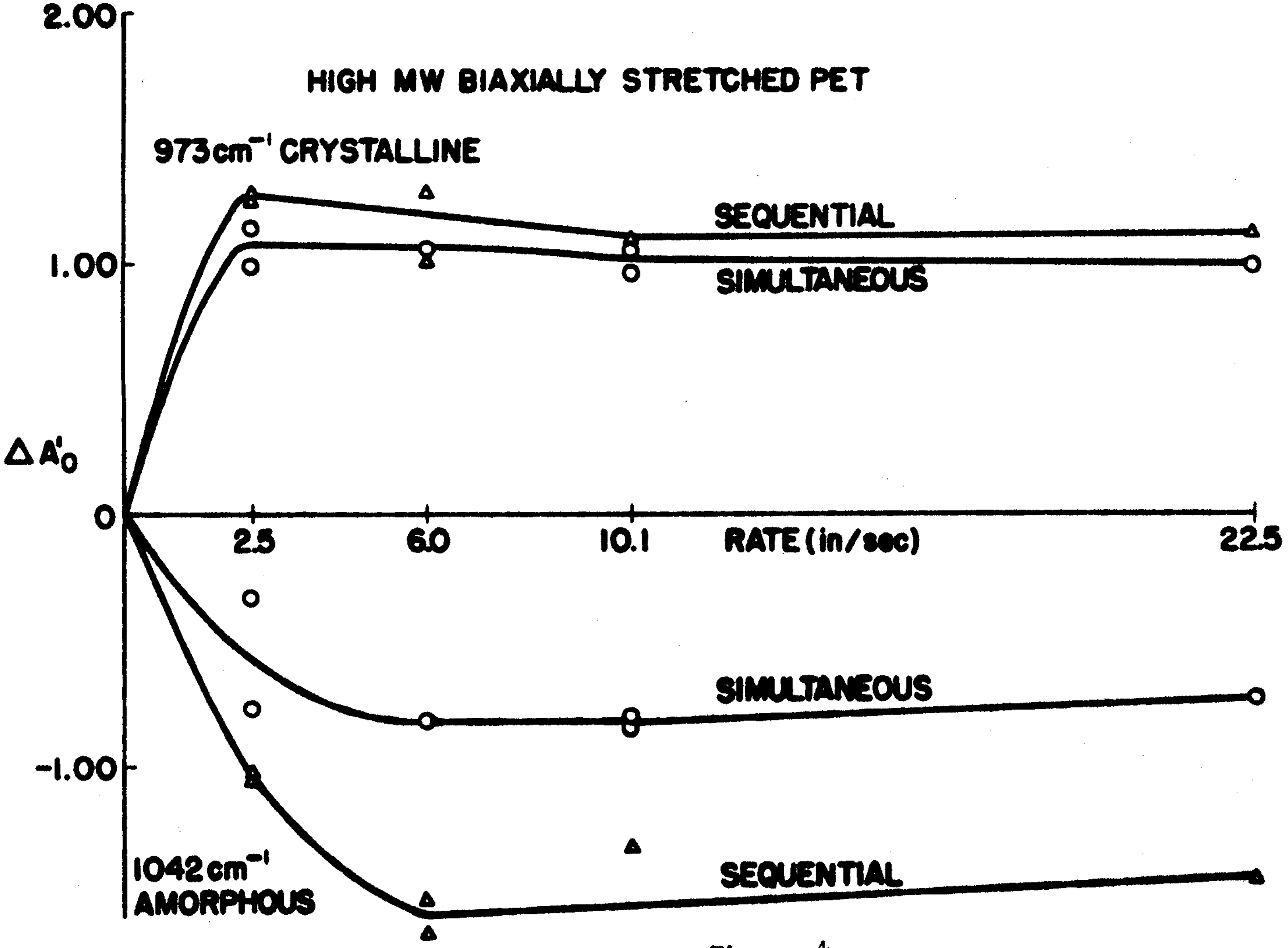
HIGH MW BIAXIALLY STRETCHED PET
973cm⁻¹ CRYSTALLINE
SEQUENTIAL
SIMULTANEOUS
SIMULTANEOUS
SEQUENTIAL
1042cm⁻¹
AMORPHOUS
ΔA'₀
2.00
1.00
0
-1.00
2.5
6.0
10.1
22.5
RATE (in/sec)

Figure 4.

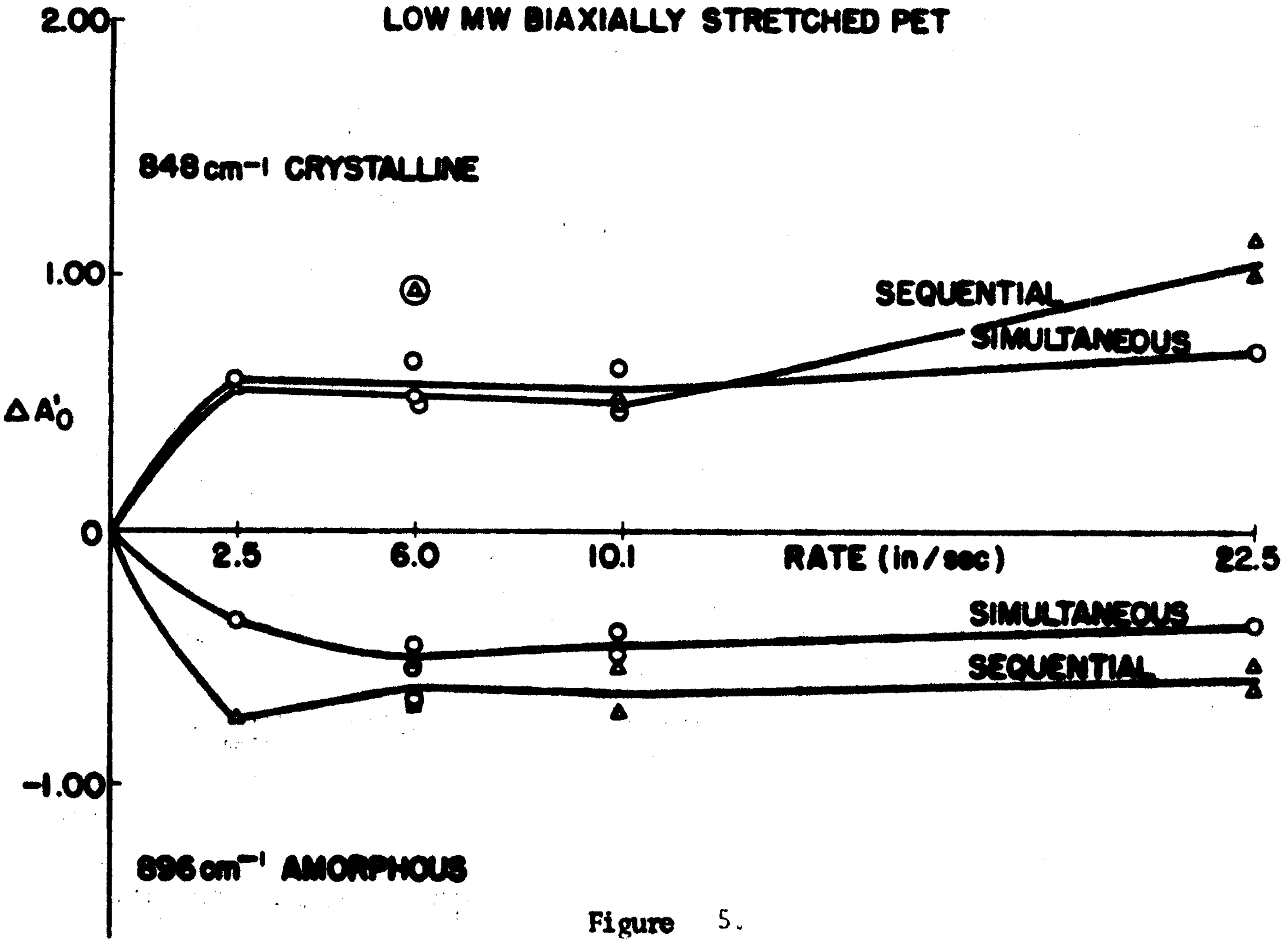
LOW MW BIAXIALLY STRETCHED PET
848 cm⁻¹ CRYSTALLINE
896 cm⁻¹ AMORPHOUS
2.00
1.00
0
-1.00
ΔA'₀
2.5
6.0
10.1
22.5
RATE (in/sec)
SEQUENTIAL
SIMULTANEOUS
SIMULTANEOUS
SEQUENTIAL

Figure 5.

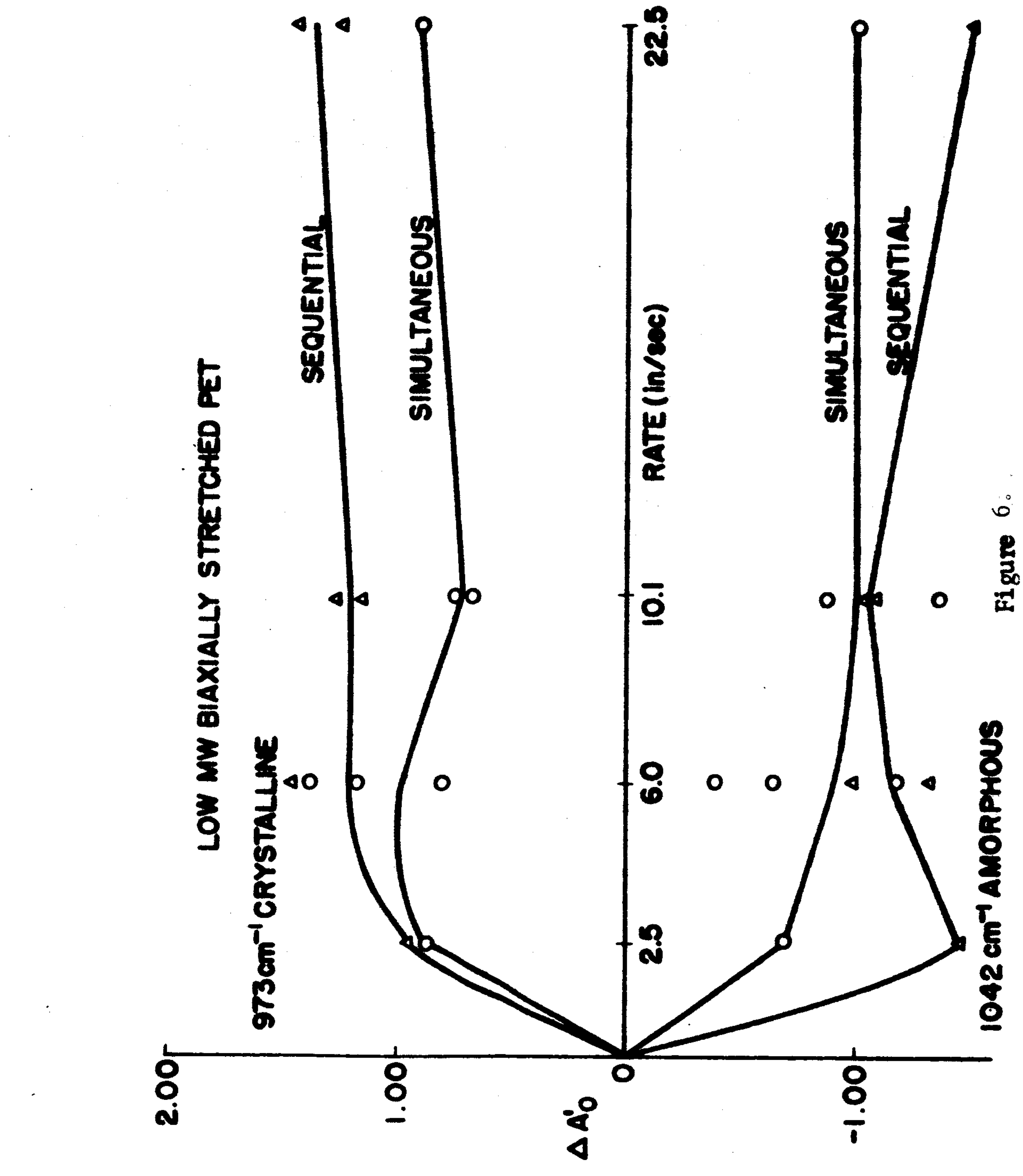
LOW MW BIAXIALLY STRETCHED PET
973cm⁻¹ CRYSTALLINE
1042 cm⁻¹ AMORPHOUS
SEQUENTIAL
SIMULTANEOUS
SIMULTANEOUS
SEQUENTIAL
ΔA'₀
2.00
1.00
0
-1.00
RATE (in/sec)
2.5
6.0
10.1
22.5

Figure 6.

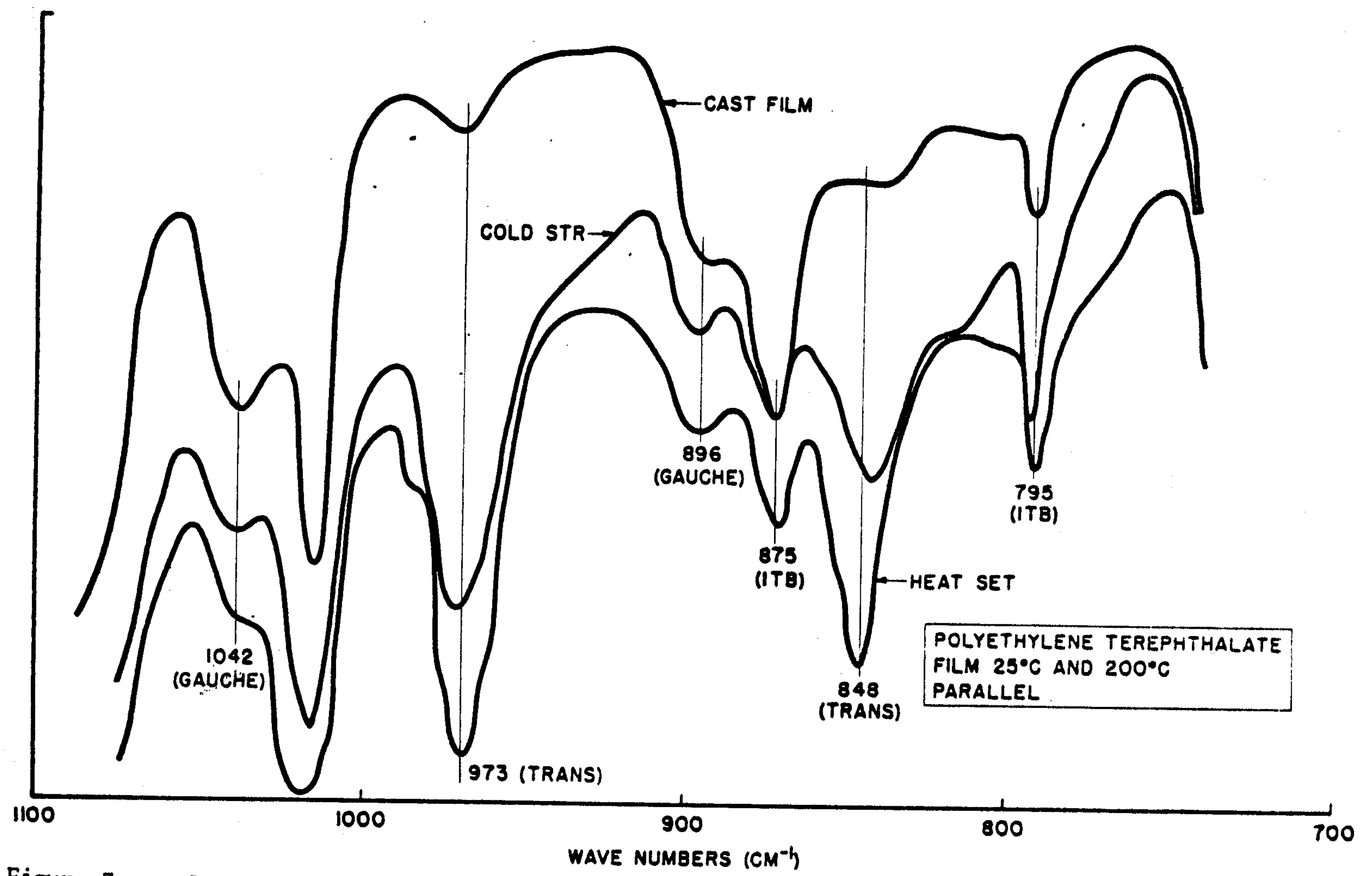

Figure 7. Spectra of Polyethylene Terephthalate Amorphous Cast Film, Cold Stretched Film and Heat Set Stretched Film.