

Yielding, Crazing, and Fracture of Polymers. II. Studies of the Retraction of Crazed and Drawn Films

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Synopsis

Optical, mechanical, and thermal data on cold- and hot-drawn as well as crazed films of bisphenol A polycarbonate suggest that three separate processes occur during deformation. These processes are a volume change, a preferential orientation of the molecules along the deformation axis, and a configurational change within the molecules (ordering). An attempt is made to correlate these processes with the various types of experimental data. It is suggested that the ordering process is activated by surface, bulk, or external stresses, which are dependent upon molecular weight, processing history, and sample geometry.

INTRODUCTION

Amorphous polymers which have been hot drawn are known to exhibit a recovery to an undrawn state when heated above their glass transition temperature.¹⁻⁵ However, it has been reported by several investigators that in dielectric and mechanical measurements on several drawn materials, an intermediate transition is observed just below their T_g .⁶⁻⁸ This transition has been associated with an orientation process in which subsequent quenching gives rise to a nonequilibrium state in the polymer, and it is this latter state which is related to the transition. It is the object of this paper to present mechanical, optical, and DSC data on cold- and hot-drawn samples as well as crazed samples of bisphenol A polycarbonate in an attempt to better understand the mechanisms by which various modes of deformation occur.

EXPERIMENTAL

Materials. Lexan bisphenol A polycarbonate resin was obtained in the form of Izod impact bars and thin film (Dr. K. Goldblum, General Electric Co., Pittsfield, Mass.). Cold-drawn samples were produced by stretching on an Instron unit at the rate of 0.2 in./min.

Hot-drawn samples were made by stretching in the temperature range 152-157°C.⁹ Crazed samples were made by soaking them in ethyl alcohol for 5 min and then stressing them on an Instron unit until crazes were

clearly visible to the naked eye. The samples were removed from the Instron unit and vacuum dried for 24 hr at room temperature.

Differential Scanning Calorimetry (DSC). DSC measurements were made with the Perkin-Elmer model instrument.

Strain Recovery. Strain recovery measurements were made with a modified Clash Berg indentation apparatus. A schematic of this apparatus is shown in Figure 1. The samples, which were in the form of pellets, were placed between two metal plates in order to give good heat

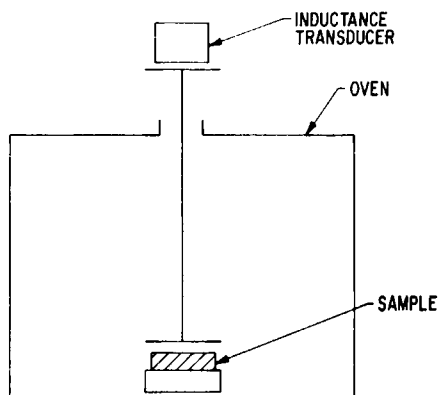


Fig. 1. Schematic of instrument used for strain-recovering measurements.

transfer from the oven to the samples. It was found that the samples came to thermal equilibrium in approximately 30 min. A Bentley transducer was used to measure the dimensional changes of the sample. Corrections were made for the normal thermal expansion of the connecting rod and the samples.

Optical Measurements. Birefringence measurements were made with a Babinet compensator in conjunction with a white light source. The fringe calibration factor was determined with the 5460-Å line of a Hg source.

Retractive Stresses. Two different systems were used to heat the samples on which the retractive forces were measured (for these measurements thin samples, i.e., 1-3 mils, were used). In one case the device for measuring the retractive force was placed in a hot air oven and the temperature was increased at different rates. A schematic of the device is shown in Figure 2. In the second system the device was placed in a hot silicone oil bath at temperature. Because of the large heat capacity of the device, the bath temperature dropped several degrees. However, a thermocouple which was mounted near the sample indicated that the sample temperature was within 1°C of the bath prior to immersion of the device. The results of these measurements in the air oven and the oil bath on similar samples were the same.

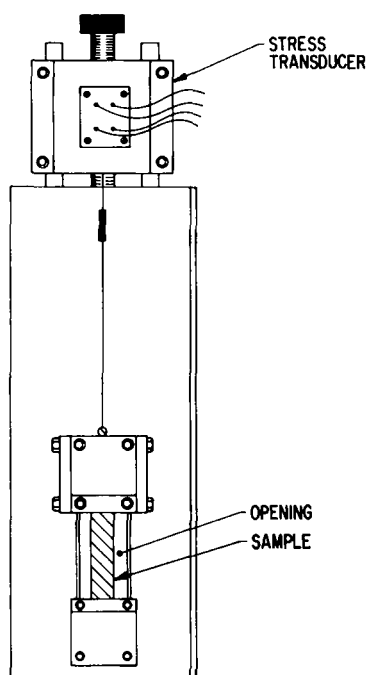


Fig. 2. Schematic of instrument used for retractive stress measurement.

Volume Temperature Measurements. The specific volume data were obtained with an automatized hydrostatic weight technique. Data were taken at temperature only after the detecting system indicated no further change in weight.

RESULTS

A typical DSC scan is shown in Figure 3 during the first heating for the samples listed in Table I. On cooling the sample to room temperature and rerunning, one obtains the second scan shown in Figure 3. The most obvious difference between these scans is the exotherm which occurs just above the T_g . This type of exotherm was found in cold-drawn, hot-drawn, and crazed samples, as well as in samples which had been annealed at temperatures less than T_g . DSC and birefringence data for several samples are summarized in Table I. By calibrating the DSC with indium, the heat released in the exotherm for these samples was calculated and is presented in Table I. In general, there does not appear to be a general relationship between the birefringence and heat release for these samples. In contradistinction to the gradual rise in the DSC curve for temperatures less than T_g , the strain and stress recovery data exhibit a very different behavior for the various types of samples, as shown in Figures 4-8.

In order to determine the thermal expansion or contraction of a crazed sample, we assumed an initial sample length L_0 and a crazed length L_c .

TABLE I

Sample no.	$\Delta \times 10^{-3d}$	T_g (1st heat), °C	T_g (2nd heat), °C	Sample wt., mg	Area cold work	$\Delta H, ^\circ$ cal/mg
1 ^a	9.95	147	141	13.4	47	0.14
2 ^a	7.2	151	147	13.1	24	0.08
3 ^a	15.4	156	145	14.5	89	0.248
4 ^b	44	157	151	15	90	0.240
5 ^a	18.6	148	143	14.6	22	0.06
6 ^a	8.6	151	148	15.7	14	0.036
7 ^c	—	153	151	14.3	8	0.02
8 ^c	—	151	149	12.6	6	0.01

^a Hot-drawn samples.

^b Cold-drawn sample.

^c Crazed samples.

^d Birefringence.

^e These values refer to entire sample.

By assuming that the uncrazed portion of a sample was unstrained, we then have

$$L = L_{u0} + \alpha_c L_{c0}$$

where L_{u0} and L_{c0} are the lengths of the uncrazed and crazed material, respectively, prior to crazing and α_c is the deformation ratio of the crazed material. Since $L_0 = L_{u0} + L_{c0}$, then

$$L = L_0 + (\alpha_c - 1) L_{c0}$$

The variation of length with temperature will now become

$$\frac{dL}{dT} = \frac{dL_0}{dT} + (\alpha_c + 1) \frac{dL_{c0}}{dT} + L_{c0} \frac{d\alpha_c}{dT}$$

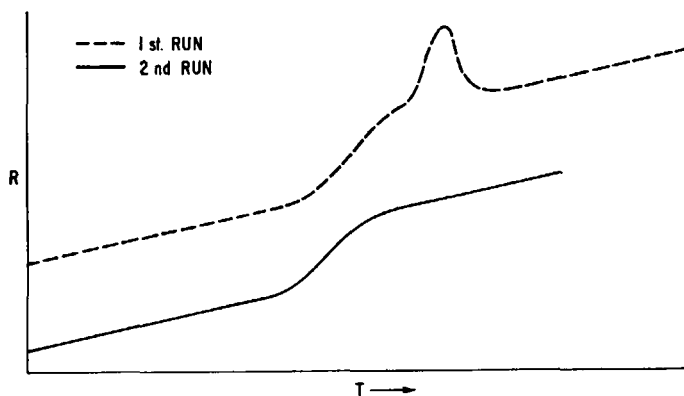


Fig. 3. Smoothed typical DSC scans for sample: broken line, 1st run; solid line, 2nd run.

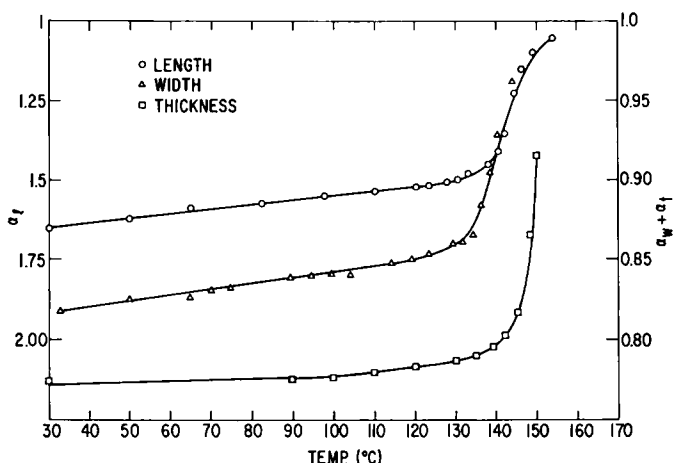


Fig. 4. Strain recovery of cold-drawn sample as a function of temperature.

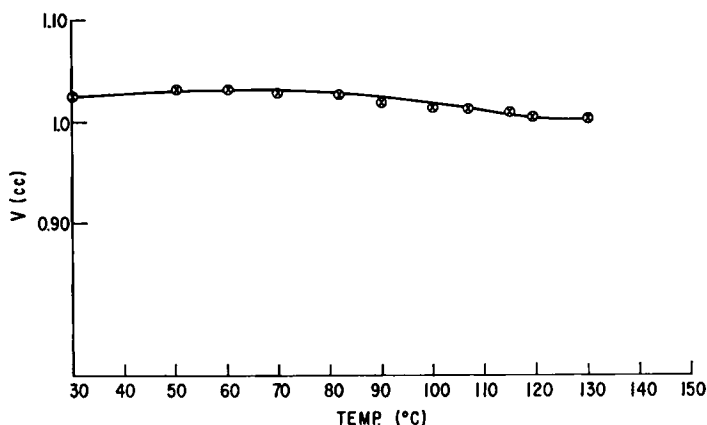


Fig. 5. Volume recovery of cold-drawn sample as a function of temperature, calculated from data in Fig. 4.

and, by dividing by the length of the sample,

$$\lambda = \frac{1}{L} \frac{dL}{dT} = \frac{1}{L} \frac{dL_0}{dT} + (\alpha_c - 1) \frac{1}{L} \frac{dL_{c0}}{dT} + \frac{L_{c0}}{L} \frac{d\alpha_c}{dT}$$

which can be rewritten as

$$\lambda = \frac{L_0}{L} \lambda_0 + (\alpha_c - 1) \frac{L_{c0}}{L} \lambda_0 + \frac{L_{c0}}{L} \frac{d\alpha_c}{dT}$$

where λ is the linear thermal coefficient of expansion. In our studies, we have found it easier to measure L initially at room temperature after crazing and then, after heating to a temperature above T_g and cooling to room temperature, to measure L_0 , which then gives $L_{c0} = L - L_0$. Since

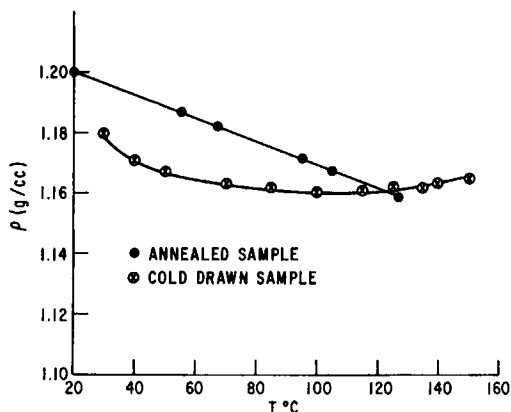


Fig. 6. Density of cold-drawn sample as a function of temperature measured by automatic hydrostatic weighing.

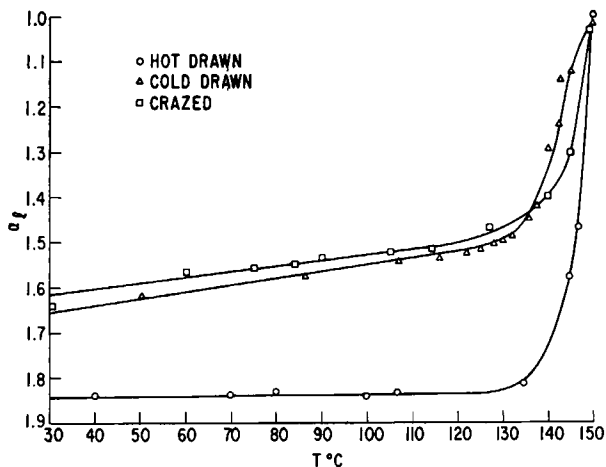


Fig. 7. Strain recovery along deformation axis as a function of temperature for hot-drawn, cold-drawn, and crazed samples.

we believed that the deformation in the craze was similar to cold-drawn material, we assumed that $\alpha(\text{crazed})$ was equal to $\alpha(\text{cold drawn})$. With this assumption, we evaluated α_c as a function of temperature and the curve is shown in Figure 7. For comparison, the results on hot- and cold-drawn samples are also shown. The remarkable similarity between the curve for the crazed and cold-drawn material might appear to be a reflection of our assumption. However, examination of samples which contain different amounts of craze material yield similar curves.

Both the DSC and the strain recovery data on the crazed samples support the assumption that the material within the craze is cold drawn.

The data obtained on the cold-drawn samples were calculated by using the final dimensions as the unstrained state.

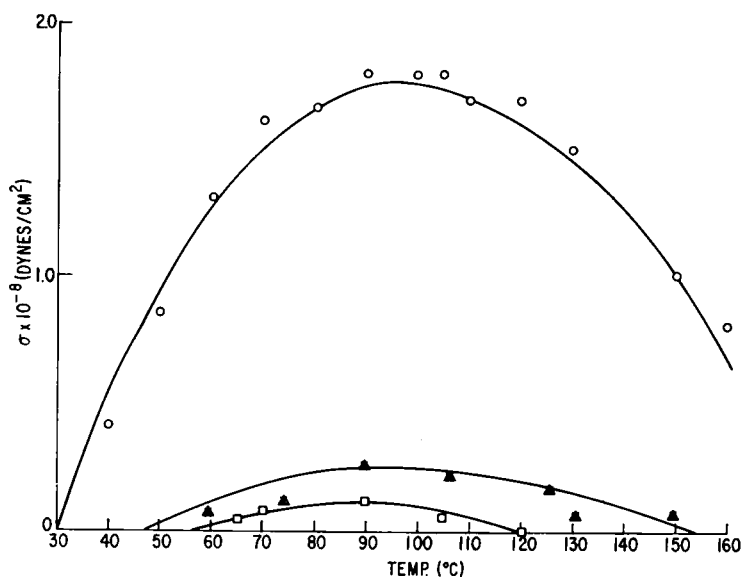


Fig. 8. Retractive stress as a function of temperature for hot- and cold-drawn samples: (O—O) cold drawn ($\Delta = 44 \times 10^{-3}$); (\blacktriangle — \blacktriangle) hot drawn ($\Delta = 13 \times 10^{-3}$); (\square — \square) hot drawn ($\Delta = 24 \times 10^{-3}$).

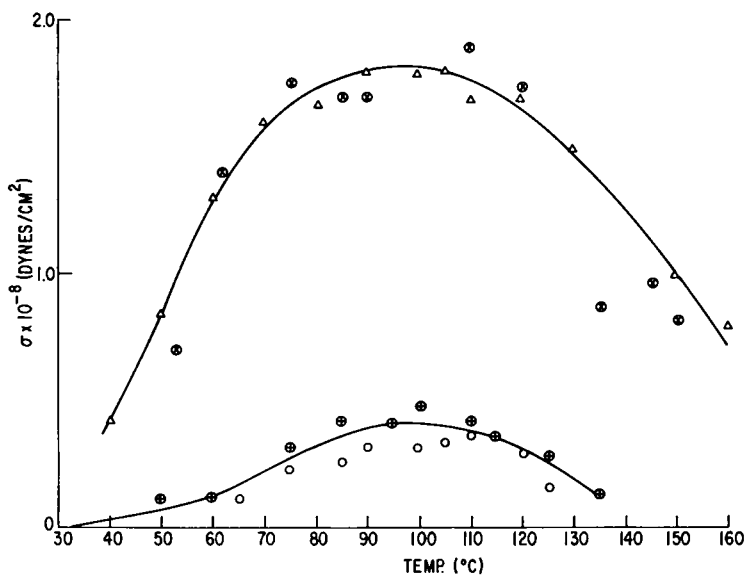


Fig. 9. Retractive stress as a function of temperature for cold-drawn and crazed samples: (1) cold drawn ($\Delta = 44 \times 10^{-3}$), (\otimes) and (Δ) points correspond to measurements in oil bath and air ovens; (2) crazed sample, (O) and (\otimes) points correspond to first and second runs on same sample.

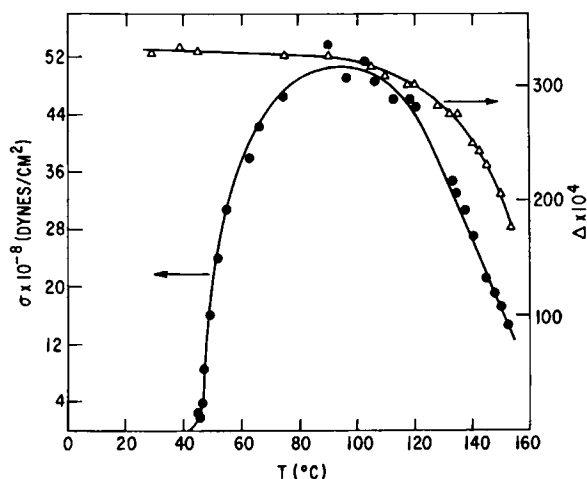


Fig. 10. Birefringence and stress as a function of temperature for cold-drawn samples.

In general, it is observed that the strain recovery and expansion data of the cold-drawn samples are consistent with the volume temperature data in Figure 7. From these data it appears that the sample is undergoing morphologic rearrangements which are reflected in the strain data. On the other hand, hot-drawn samples do not appear to exhibit this behavior. The retractive force data shown in Figures 8 and 9 exhibit a maximum approximately 40°C below the T_g for the samples. The magnitude of these force maxima does not correlate with either the initial birefringence or the heat release. In fact, the value of the birefringence during these experiments does not relax significantly until the force begins to decrease near T_g .

DISCUSSION

The variation in the stress and strain recovery displayed in Figures 4, 6, 8, and 9 suggests that two mechanisms are operative. At temperatures below the maximum in the stress temperature curves, denoted by T_s , the stress increase occurs because the sample tends to contract along the original deformation axis. As we increase the temperature above the T_s , we believe the sample would still tend to contract, yet the stress begins to decrease. Careful examination of the samples that gave the highest stress maxima (1.8×10^8 dynes/cm²) during the experiment indicated that the decrease in stress above T_s was due to a local yielding of the sample. We were unable to detect a similar yielding in the other samples, and yet a stress maximum is observed. If we assume that these latter samples are undergoing a homogeneous rather than local yielding, then the force maxima are a reflection of the yield stress of the different samples. Since the magnitude of the stress maximum does not appear to be directly related

to the birefringence of the sample, we believe, as already noted elsewhere, that preorientation does not affect the yield stress directly, but in some way affects the packing density and configurational ordering of the molecules.¹⁰ On the basis of the data obtained in this study, we believe that the process of cold drawing involves three morphologic changes in the sample structure: a preferential orientation of the molecules along the deformation axis, a conformational change within the molecule, and a change in the packing density. We use the following arguments to support this position.

The volume recovery as well as the strain recovery data on cold-drawn and crazed samples in contrast to both hot-drawn and annealed samples indicate that these samples undergo an extra expansion in the same temperature where the force begins to rise sharply, while the birefringence and DSC scan do not indicate any marked change. Since the birefringence is a direct measure of the orientation and will not be affected by isotropic volume changes, we conclude that the changes noted below the T_g must be related to packing density.

Since the magnitude of the exotherm which is observed above T_g does not appear to be directly relatable to the orientation, as measured by birefringence, and can be obtained by annealing the sample at temperatures below T_g , this effect must be part of the same ordering process which we previously described.¹⁰ If this interpretation is correct, then the process of recovery of drawn samples must involve at least three separate and distinct processes. The first process, which is measured by the birefringence of the sample, involves a disorientation of the molecules with respect to the drawing axis; the second process involves a configurational entropy change within the molecules; and the third process involves a volume relaxation effect. On the basis of our data, it appears that volume change occurs primarily below the T_g , the disorientation, at T_g , and the configurational entropy change, above T_g .

Since the volume change below T_g can be related to an entropic effect by the following thermodynamic relation

$$\Delta S = \left(\frac{2P}{2T} \right)_g \Delta v$$

where $(2P/2T)_g$ is the thermal pressure coefficient, one would expect to observe a similar effect in the DSC curves. We believe that the DSC is not sensitive enough to determine this because the volume change is very small and spread over a broad temperature range. Thus, the exotherm which occurs above T_g on annealed, cold-drawn, hot-drawn, and crazed samples reflects a distinct type of ordering. Attempts to produce exotherms by annealing samples which had been held at 170°C for 30 min and then quenched to 5°C above their T_g were not successful, and yet samples annealed between 80°–140°C (approximately 10°C below their T_g) all gave exotherms. This result can be rationalized if one assumes that this ordering process is stress activated either by surface, bulk, or external

stresses, and could be used to explain some of the differences between the works of other investigators, because the magnitude of such stresses would be dependent not only on the processing history and molecular weight of the sample but also on sample geometry, specifically thickness.^{11,12} Since the disordering process must be dependent on similar variables, further comparison and speculation of such data are not warranted at this time.

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