

Thermal Shrinkage of Drawn Polystyrene

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Synopsis

Many papers have reported on the thermal shrinkage mechanism of drawn polymers. The cause of the thermal shrinkage is very complex, because that relates to many factors. In this study, atactic polystyrene, a noncrystalline polymer, was used to eliminate factors related to the melting and crystallization effects, and it is considered that there is a relation between the change of the polymer's structure due to heat treatment and thermal shrinkage. It is observed in a certain temperature range that the thermal shrinkage of drawn polystyrene is not caused by increase of the entropy but results in decrease of the entropy.

INTRODUCTION

It is generally well known that polymers are widely used for raw materials in industry. An information of the dimensional stability for heat treatment (i.e., thermal shrinkage) is required for use in industry, the same as that of mechanical properties. Therefore, many papers have been published on the mechanism of the thermal shrinkage of polymers.¹⁻¹⁵ These studies suggest several cause of the thermal shrinkage, related to the decrease of the degree of orientation of extended polymer chains in amorphous region, to the melting behavior of a crystal, and to crystallization of the polymer chain. The mechanism of thermal shrinkage is not simple but complex because several factors are related.

In this study, atactic polystyrene (PS) was used to eliminate the factors related to melting and crystallization effects. The object of this paper is to observe a relation between the thermal shrinkage and change of physical properties in shrunked samples, and to investigate the mechanism of thermal shrinkage. The information obtained for noncrystalline polymers is applicable to practical use of polymer materials and polymer process.

EXPERIMENTAL

(1) Sample preparation: "Styrene 666" supplied by Asahi Dow Co. Ltd. (molecular weight was 1,000,000 and $M_n/M_w = 2.9-3.0$) was used for samples in our experiments. Polystyrene pellets were pressed at 170°C and quenched in ice water to form films. Each film was drawn in an air oven at 130°C at a rate of 4%/min. Change of thickness before and after drawing was shown approximately as follows:

$$\begin{aligned} &(\text{thickness before drawing})/(\text{thickness after drawing}) \\ &= [(\text{length after drawing})/(\text{length before drawing})]^{1/2} \end{aligned}$$

(2) Birefringence measurement: Retardation in sodium D line (589 nm) was measured using a polarized microscope with Berek compensator.

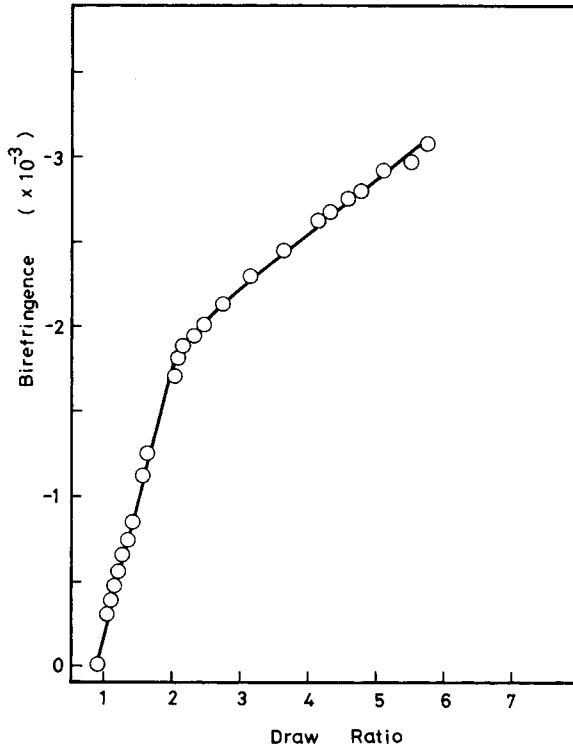
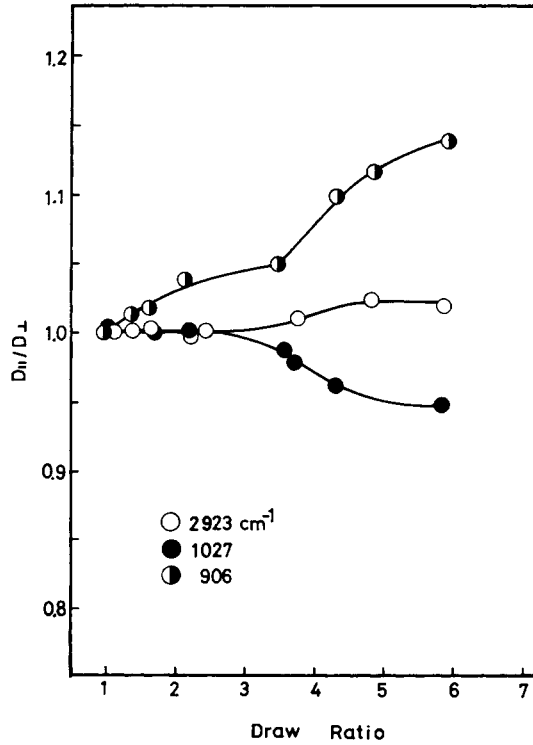


Fig. 1. Change of birefringence with draw ratio.

Fig. 2. Change of dichroic ratio ($D_{||}/D_{\perp}$) with draw ratio.

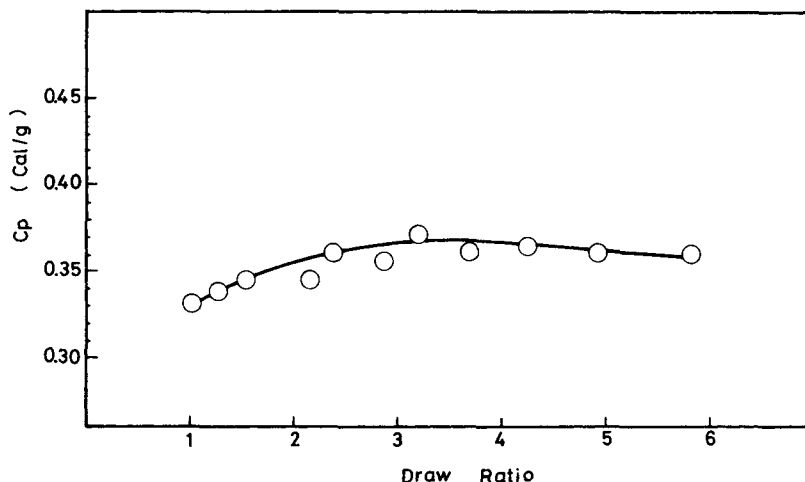


Fig. 3. Change of specific-heat capacity (C_p) at 330 K with draw ratio.

(3) Measurement of specific-heat capacity at constant pressure (C_p): The specific-heat capacity C_p was measured in 1 atm. at a heating rate of $5^\circ\text{C}/\text{min}$ over a temperature range of 320–380 K using a differential scanning calorimeter (DSC-2 type, Perkin Elmer Co. Ltd.).

(4) Infrared dichroism measurement: Infrared spectrometer, Hitachi EPI-2 type equipped with AgCl polarizer was used for an infrared dichroism measurement. Imperfect polarization was corrected according to our method which has been reported previously.¹⁶ The orientation of the main chain of polymer was calculated from the dichroism of 2923 cm^{-1} CH_2 absorbance.^{17,18} Both bands of 1027 and 906 cm^{-1} were used for studying the orientation of phenyl group in side chains.

(5) Method of heat treatment and definition of shrinkage: The change of sample length was measured by a measuring microscope. The draw ratio, shrinkage ratio, recovery ratio, changing ratio of birefringence are defined as follows: draw ratio (λ) = l_d/l_0 , shrinkage ratio ($S\%$) = $[(l_d - l_s)/l_d] \times 100$, re-

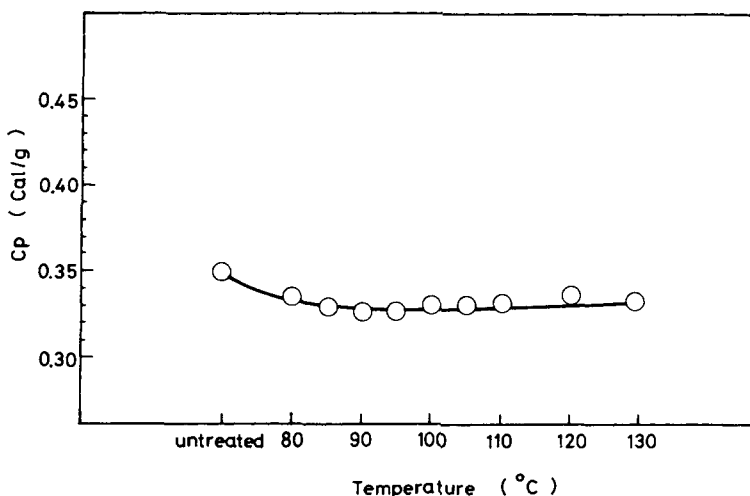


Fig. 4. Change of specific-heat capacity (C_p) at 330 K with heat-treated temperature.

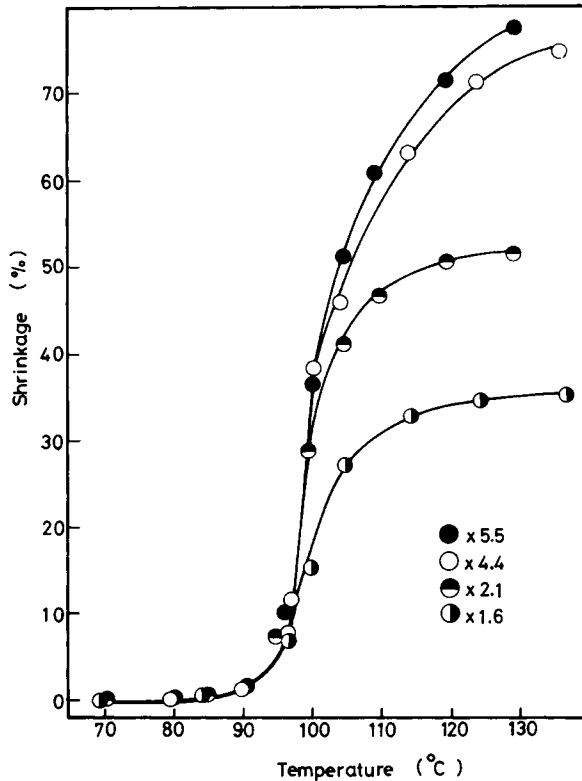


Fig. 5. Change of shrinkage percent with heat-treated temperature.

covery ratio ($R\%$) = $[(l_d - l_s)/(l_d - l_0)] \times 100$, change ratio of birefringence ($\Delta N\%$) = $[(n_d - n_s)/(n_d - n_0)] \times 100$, where l_0 is the length before drawing, l_d is the length after drawing, l_s is the length after heat treatment, n_0 is the birefringence before drawing, n_0 is the birefringence before drawing, n_d is the birefringence after drawing, and n_s is the birefringence after heat-treatment.

The percent shrinkage increases gradually with time when the drawn samples are heat treated at temperatures below 130°C. In the experiment each sample was wrapped with aluminum foil and heat treated in a silicone oil bath for 15 min.

RESULTS AND DISCUSSION

Figure 1 shows a change of the birefringence by drawing, as a function of draw ratio. When the main chain of PS is stretched in the draw direction, the phenyl group (side chain of PS) is arranged in normal to the draw direction as seen from the molecular structure. The drawn samples show a negative birefringence since the refractive index of the phenyl group is larger than that of the main chain. The birefringence increases quickly as the draw ratio increases twice the initial length, and then slowly increases.

Figure 2 shows a change of the dichroic ratio (D_{\parallel}/D_{\perp}) by drawing, where D_{\parallel} and D_{\perp} are the absorbance of a radiation polarized in parallel and perpendicular to the chain axis, respectively. The dichroic ratio in the 2923 cm^{-1} band scarcely changes by drawing, though increases a little for draw ratios above 2.5. The 1027

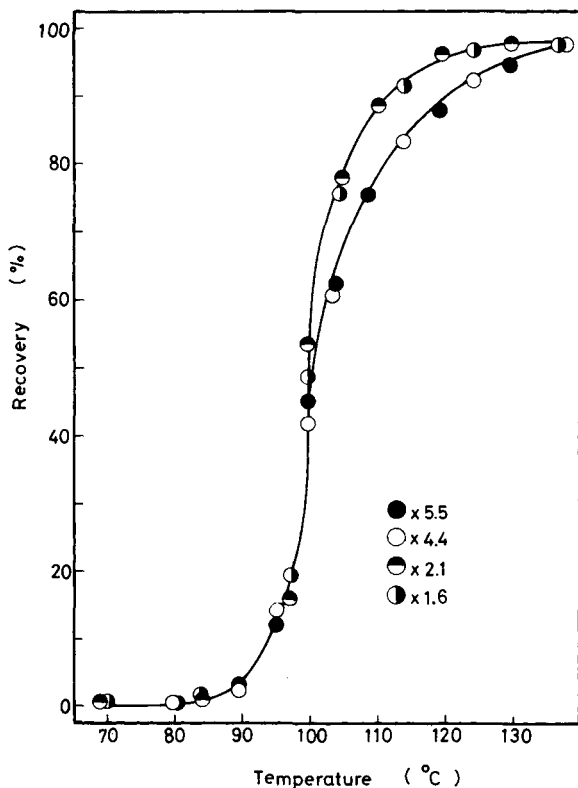


Fig. 6. Change of recovery ratio with heat-treated temperature.

cm^{-1} band is the vibration in benzene ring plane and shows perpendicular dichroism ($D_{\parallel} < D_{\perp}$) if the plane of benzene ring is aligned perpendicular to the surface of the film by drawing. The D_{\parallel}/D_{\perp} of 1027 cm^{-1} decreases a little with increase of the draw ratio. Figure 2 shows that the D_{\parallel}/D_{\perp} in 1027 cm^{-1} decreases for the draw ratios of more than 2.0, i.e., the orientation of the phenyl group increases for these draw ratios.

The 906 cm^{-1} band is out of benzene ring plane and shows parallel dichroism ($D_{\parallel} > D_{\perp}$). The D_{\parallel}/D_{\perp} of 906 cm^{-1} band increases with the increase of draw ratios. The results show that the orientation of the phenyl group increases for draw ratios of more than 2.0.

Figure 3 shows a change of the specific-heat capacity. The C_p increases at the beginning of drawing, passes through a maximum at a draw ratio of 3.0, and then decreases. This tendency is very different from that of a natural rubber, whose C_p decreases monotonously with drawing.¹⁹⁻²¹

Figure 4 shows a change of C_p with heat treatment. The C_p decreases by heat treatment at lower temperatures than 90°C , and scarcely increases at higher temperatures than 90°C .

A relation of the heat-treatment temperature with the shrinkage ratio is shown in Figure 5. The shrinkage begins at 85°C and increases suddenly at 92°C . The length of each sample returns to its original length at 130°C .

The change of the recovery ratio as a function of heat-treating temperature is shown in Figure 6. Term "recovery" means recovery of the length to the original. Figure 6 shows that the recovery-treating temperature curves of highly

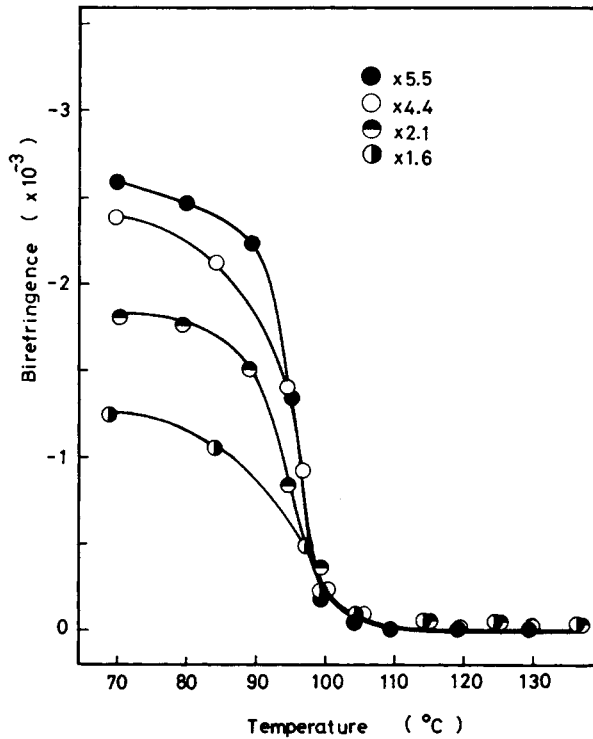


Fig. 7. Change of birefringence with heat-treated temperature.

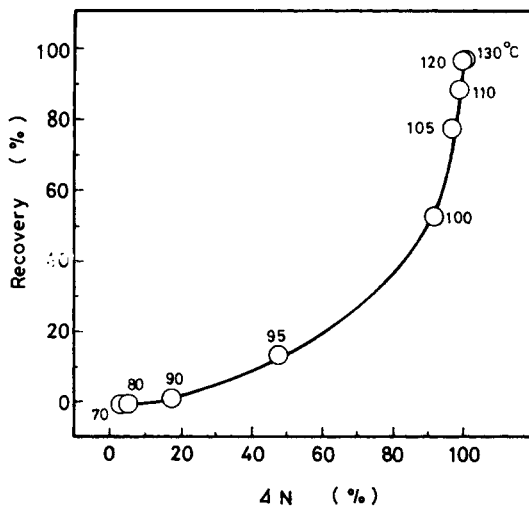


Fig. 8. Relation between change ratio of birefringence (ΔN) and recovery ratio.

stretched samples with draw ratios of 5.5 and 4.4 have identical shapes, and the low stretched samples with draw ratios of 1.6 and 2.1, are different from them.

Figure 7 shows a relation between the birefringence and the heat-treated temperature. The birefringence begins to decrease at a temperature lower than that at which the thermal shrinkage begins. The orientation of each sample

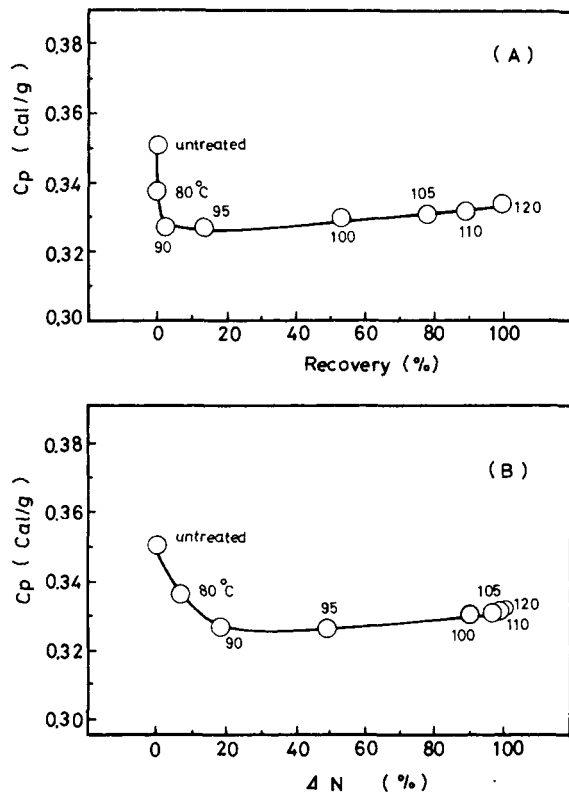


Fig. 9. (A) Relation between specific-heat capacity (C_p) at 330 K and recovery ratio. (B) Relation between C_p at 330 K and change ratio of birefringence (ΔN).

begins to decrease at 80°C, and zero at 105°C, corresponding to its original state, though the recovery ratio does not reach 100% at 105°C. The birefringence of the sample heat treated at 105°C is zero, while the recovery ratio is about 60% and 80% of highly and low stretched samples, respectively. That is to say, Figures 6 and 7 indicate that the samples do not recover their original length in spite of zero orientation.

Figure 8 shows a relation between the change ratio of the birefringence and recovery ratio. It is seen from Figure 8 that there is three regions on the thermal shrinkage of drawn PS: first where the orientation of the sample falls but the sample does not shrink, second where decrease of the orientation and increase of the shrinkage are observed, and third where the sample shrinks by heat treatment, though the birefringence is almost zero, i.e., the sample has no orientation.

A relation between C_p and the recovery is shown in Figure 9(a), and the relation between C_p and the change ratio of the birefringence is shown in Figure 9(b). The thermal shrinkage is not observed below 90°C, though C_p decreases considerably. Above 90°C the shrinkage increases remarkably, but C_p is almost unchanged as shown in Figure 9(a). Figure 9(b) shows that decreases of C_p and birefringence are observed below 90°C and that the birefringence decreases remarkably above 90°C in spite of invariant of C_p . From the results, the mechanism of thermal shrinkage is considered as follows: In the first region, both C_p and birefringence decrease but thermal shrinkage does not yet occur. In the

second region, the thermal shrinkage begins to occur and the decrease of the orientation is remarkable, but C_p does not change. In the third region, the thermal shrinkage increases and C_p slightly increases with increase of the heat-treating temperature though birefringence is almost zero.

T_g was measured with differential scanning calorimeter. It was determined from the DSC curve as the intersection of the extension of the base line with a line tangent to the maximum slope of endothermic peak and was observed at 90°C.

The first region is in the temperature range below T_g . The segmental motion of the main chain do not occur in this range of the first region, however, both the motion of the phenyl group and the local oscillation mode of the main chains are observed in this temperature range.^{22,23} The decrease of the birefringence may be related to the decrease of the orientation of benzene ring aligned in the direction perpendicular to the chain axis. It is considered that the change of orientation in benzene ring has no effects on the thermal shrinkage. The stress of intermolecular and intramolecular chains caused by drawing is released by the motion occurred below T_g , and the state of the sample returns to be stable to result in decrease of C_p .

The second region is above T_g , and the segmental motion of the main chain is allowed. Therefore, a remarkable decrease of the orientation and the shrinkage are observed in this region. The shrinkage may be related to the decrease of the orientation of the main chain, while C_p remains unchanged. This fact suggests that the shrinkage of drawn PS is quite different from that of the natural rubber and may not result from the increase of the entropy which causes the natural rubber to shrink, though the shrinkage of both samples is related to the decrease of the orientation on the main chain.

Entropy (ΔS) is defined as follows:

$$\Delta S = \int C_p/T dT$$

In this experiment, C_p is measured over a temperature range from 325 to 365 K. C_p temperature curves do not intersect each other in the temperature range. Therefore, the change of C_p with heat treatment or drawing is reflected in the change of entropy without calculation of entropy by use of C_p .

Under the drawing condition in the experiment, the C_p of PS increases by drawing, unlike decrease of the natural rubber's C_p . It is reasonable that the thermal shrinkage of drawn PS is not caused by the increase of the entropy.

The drawn PS shrinks in the third region, while the orientation is nearly zero, and the C_p somewhat increases. It is considered that the thermal shrinkage in the region is caused by the entropy change, since a slight increase of C_p is observed. Though the polymer chains were randomly arranged in the second region, a more stable state may be formed by the heat treatment in the third region and then the C_p increases slightly.

CONCLUSION

The thermal shrinkage of the drawn polystyrene does not result from the entropy change, unlike that of rubber, but is mainly caused by reduction of the orientation of the polymer chains. The thermal shrinkage without the decrease of the orientation is caused by forming a more stable state in the amorphous region.

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Received May 17, 1977

Revised July 29, 1977