

# THE EFFECT OF HOT DRAWN ON THE PHYSICAL AGING OF ATACTIC POLYSTYRENE\*

SONG Rui (宋 锐) LIN Xin (林 辛) CHEN Jing (陈 晶)

GAO Jingui (高金贵) and FAN Qingrong (范庆荣)

(Polymer Physics Laboratory, Institute of Chemistry, Chinese Academy of Sciences,  
Beijing 100080, China)

**Abstract** The physical aging behavior of atactic polystyrene (aPS) films achieved under different drawing conditions has been studied by optical birefringence and modulate differential scanning calorimeter (m.d.s.c.). The results show that on annealing at specific temperature below glass transition temperature ( $T_g$ ), the enthalpy relaxation ( $\Delta H$ ) and  $T_g$  decrease with increasing of birefringence ( $\Delta n$ ). On the other hand, the effect of molecular draw ratio (MDR) is confusing:  $\Delta H$  and  $T_g$  decrease with increasing of MDR in the early stage of aging, but the MDR's effect become unobvious with the development of aging. It may be concluded that the ordered domain generated by the drawing below or above glass transition temperature will affect the development of physical aging behavior. The viewpoint of cohesive entanglement is used to account for the above observations.

**Keywords** Modulated differential scanning calorimetry (m d.s.c.); Atactic polystyrene; Physical aging; Extension; Orientation

## INTRODUCTION

Physical aging of glassy polymers has been studied by various measuring techniques such as impact testing, differential scanning calorimetry, infra-red spectroscopy, tensile testing, dynamic mechanical spectroscopy, X-ray diffraction method, fluorescence spectroscopy, electron spin resonance spectroscopy and positron annihilation lifetime spectroscopy, etc<sup>[1]</sup>, and the results have been the subjects of reviews, papers, and books indicating that this phenomenon would exert an unnegligible effect on the performance of polymeric materials.

Amongst the polymeric materials that have been studied, atactic polystyrene (aPS) has been the one that deeply arouse men's interest as it is a well known polymer with important industrial applications and theoretical significances. Although

\* This work was Supported by the National Basic Research Project-Macromolecular Condensed State.

Received April 28, 1997

the physical aging of aPS has been studied in great detail, the effect of draw condition on physical aging phenomena has not yet brought to our enough attention, very few studies on this subject can be found in the literatures. In fact, draw or orientation processes, as the most conventional way to obtain the final products, would inevitably play an important role in the physical aging of aPS.

In the present work, we studied the physical aging behavior of samples with different extension and orientation, in order to relate the presented orientation in the materials with the following aging performances.

## EXPERIMENTAL

### *Materials*

The atactic PS granulate is provided by Jiamusi Synthetic Materials Factory, P.R. China, with number average molecular weight  $M_n = 8.2 \times 10^4$  (determined by GPC-210, Polymer Laboratories). PS samples for ensuing tests were cast into films from a 7.8% toluene solution with an average thickness of  $150\mu\text{m}$ .

Oriented samples from thin films were obtained on an apparatus developed in this laboratory, i.e. a stretching machine operating at variable strain rate and with a special oven to maintain a rather constant temperature (within  $\pm 0.5^\circ\text{C}$ ) over all the sample. Draw ratios were determined by measuring the distance between ink marks on the sample. Different strain rates (from 0.21/min to 1.78/min) and stretching temperature (from 85 to  $135^\circ\text{C}$ ) were used. Thereafter, specimens were air quenched below  $T_g$ , then they were maintained at a sub- $T_g$  annealing temperature for different time (from 26 to 257 h). In order to retain the original orientation,  $78^\circ\text{C}$ , which was rather lower than  $T_g$  ( $100^\circ\text{C}$ , detected by d.s.c at  $20^\circ\text{C}/\text{min}^{-1}$ ), was selected as the aging temperature and the samples were kept at constant length during the aging treatment.

### *DSC test*

Differential scanning calorimetry (d.s.c.) was carried out on a Model 2910 m d.s.c. cell and a DuPont Thermal Analyst Model 2100 based on an IBM PS/2 Model 60 computer. Excellent review of this technique can be found in Ref.[2] and a typical m d.s.c curve of aged aPS sample was illustrated in Fig.1. A heating rate of  $5^\circ\text{C}/\text{min}$ , an oscillation amplitude of  $0.8^\circ\text{C}$  and an oscillation period of 40s were used throughout this investigation. These modulation parameters were chosen so that the heating rate was always above zero, i.e. no cooling occurred during the scanning process for the temperature region of interest. In order to

maximize the signal as well as to reduce the heat transfer delay, an average sample weight of about 10 mg was used, with an empty pan as the reference. Indium was used to rectify the temperature and energy. The heat capacity calibration was made by running standard sapphire sample over a wide temperature range and comparing the determined heat capacities with the literature values. 30°C and 140°C were selected respectively for the initial and final temperature of the scanning measurement. Nitrogen purge of 40 mL/min was used for all samples.

The enthalpy relaxation  $\Delta H$ , which defined as the relative departure of aging polymers from glassy polymers, was estimated from m.d.s.c. thermograms by measuring the area enclosed between the traces of peak that showed in the non-reversible heat-flow curves.  $T_g$  was defined as the inflection point in the reversible heat-flow curves.  $T_{max}$  was taken as the maximum position of endothermic  $C_p$  peak in the same curves as that of  $\Delta H$ . The details can be found in Fig. 1.

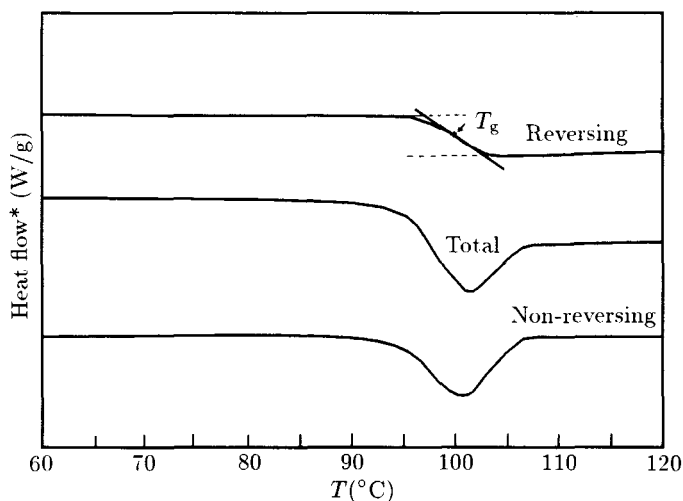


Fig. 1 The typical m.d.s.c. curves indicating the reversible and non-reversible heat flow of a drawn aPS film

### Birefringence

Birefringence can reflect the extent of all segment orientation in the polymer system. The orientation of the samples was characterized by using optical anisotropy measurements<sup>[3]</sup>. The difference between refractive indexes ( $\Delta n$ ) parallel and perpendicular to the draw direction were measured by using an Abbe refractometer (Model WZS-1, Shanghai), illuminated by monochromatic light ( $\lambda = 589$  nm) from a sodium vapor lamp. To avoid scattering of light from the surface, cinnamon oil (refractive index=1.590~1.610 at 20°C) was used as immersion fluid, all the measurements were conducted at room temperature (ca. 16°C).

*Molecular draw ratio*

Due to viscous chain slippage or relaxation during drawing, the nominal draw ratio (DR) cannot always express the molecular draw ratio, the efficiency of draw can be measured by elastic recovery of drawn samples<sup>[4]</sup>.

$$\text{MDR} = (L_t - L_s)/L_0 + 1 = \Delta L/L_0 + 1$$

$L_t$  is the total length after draw,  $L_s$  is the shrunken length of a drawn sample heated well above its  $T_g$ . The MDR of the samples was measured at room temperature by using a measuring microscope, Model JXD-12.

The bulk densities ( $\rho$ , g·cm<sup>-3</sup>) of the film specimens were measured at 21°C in a density gradient column containing isopropyl alcohol/diethylene glycol. The column had a density measurement range from 1.02~1.08 g·cm<sup>-3</sup> with the density accuracy of 0.0001g·cm<sup>-3</sup>.

**RESULTS AND DISCUSSIONS**

First we investigate the temperature dependence, Table 1 showed the samples obtained under different drawing temperatures, all the resulting films have nearly the same draw ratio (DR) and draw speed.

**Table 1** Preparation of drawn aPS samples at different drawing temperatures

| Draw temperature* | MDR  | $\Delta n(\times 10^3)$ | Density (g. cm <sup>-3</sup> ) |
|-------------------|------|-------------------------|--------------------------------|
| 85                | 1.38 | 214.2                   | 1.0468                         |
| 95                | 1.47 | 201.1                   | 1.0482                         |
| 100               | 1.54 | 174.5                   | 1.0480                         |
| 105               | 1.69 | 126.1                   | 1.0471                         |
| 110               | 1.82 | 106.4                   | 1.0471                         |
| 115               | 1.51 | 88.0                    | 1.0474                         |
| 120               | 1.39 | 34.6                    | 1.0465                         |
| 125               | 1.24 | 10.2                    | 1.0469                         |
| 130               | 1.20 | 1.6                     | 1.0475                         |
| 135               | 1.16 | 0.8                     | 1.0477                         |

\* Draw speed =0.12/min; Draw ratio=1.22

Owing to the intrinsic brittleness especially near or below  $T_g$ , the samples were obtained under relatively low draw speed and were drawn up to only DR=1.24. Unsimilar to crystallizable polymers, such as poly(ethylene terephthalate) (PET), drawing can not give rise to any obvious density increase. It can be noted that,

MDRs, which could be regarded as the efficiency of draw or orientation of molecular scale, were varied but have a maximum with increasing of drawing temperatures; whereas the  $\Delta n$ , which could be taken as the degree of segmental orientation in general sense, shows a decreasing tendency with increasing of drawing temperature. Then at constant temperature, the obtained samples were subjected to aging for different time. Fig. 2 and Fig. 3 showed the effect of aging time on the enthalpy relaxation  $\Delta H$  and  $T_g$ , respectively.  $\Delta H$  increases as a linear function of  $\log t_a$  ( $t_a$ , aging time) and the  $T_g$  moves towards higher temperatures with increasing of aging time, these behaviors are well established features of physical aging for glassy polymers as observed by others<sup>[9,10]</sup>.

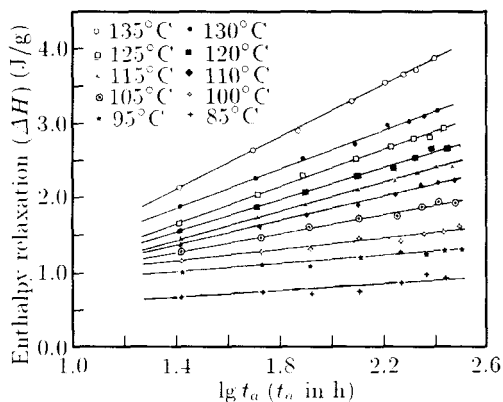


Fig. 2 Enthalpy relaxation  $\Delta H$  vs. logarithmic aging time ( $\log t_a$ ) for aPS films obtained at different drawing temperatures  $T$  as indicated

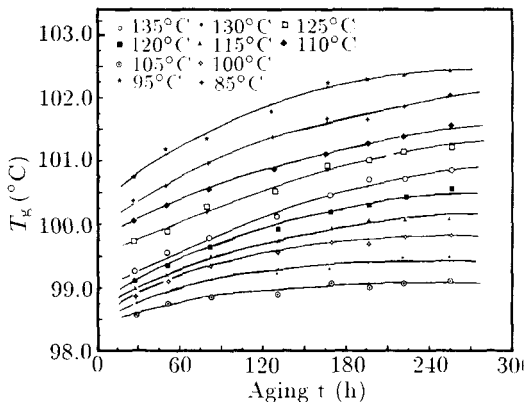


Fig. 3 Effect of aging time on glass transition temperature ( $T_g$ ) for aPS films obtained at different drawing temperatures  $T$  as indicated

Then it is interesting to note that all the specimens, which have nearly same draw ratio and density, display different physical aging behavior, why? What is the main reason that responsible for this result? Under same draw ratio and draw speed, MDRs changed saddle-like with the drawing temperatures,  $\Delta n$  showed the decreasing tendency with temperature increasing, as details that were depicted in Fig. 4, there was a maximum MDR in the vicinity of 115°C.

This observation is comprehensible because the drawing is a process in which orientation and relaxation (tend to disorientation) can take place instantaneously, the final effect is dependent on the drawing condition. A number of studies have shown, that if the temperature is relatively high (above  $T_g$ ) and the strain rates is low, stretching without resultant orientation may occur, this is called flow drawing<sup>[5]</sup>. It was suggested that under these condition, molecular relaxation processes predomi-

nate over the orientation process. Consequently, the drawing tension drops to low levels and results in flow drawing. It has also been suggested that above certain critical temperature, the intermolecular linkages are broken down, and as a result of which the polymer molecules may slip over one another and flow individually, exhibiting a large deformation without inducing any molecular orientation just like in flow of a simple liquid.

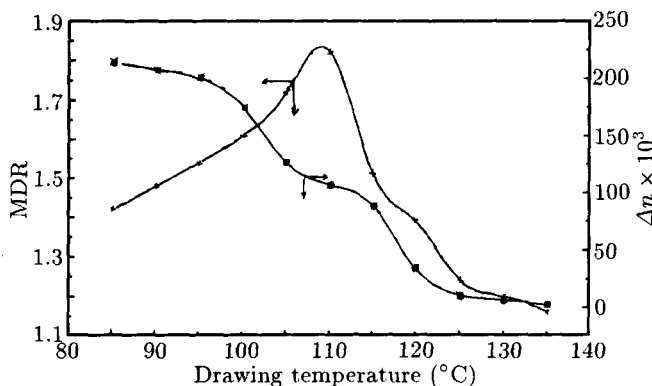


Fig. 4 The drawing temperature dependence of MDR and  $\Delta n$  for aPS films

Fig. 5 shows clearly that the  $\Delta H$  and  $T_g$  are the functions of  $\Delta n$ , the  $\Delta H$  and  $T_g$  all decrease monotonically with the increasing of  $\Delta n$  of samples. Three periods of aging time, 26, 124 and 257 h, corresponding to early, intermediate and final phase of aging in these investigation respectively, were selected to explicate the effect of  $\Delta n$  on the aging behaviors. In the same way,  $\Delta H$  and  $T_g$  were plotted against MDR of drawn samples. In early stage of aging,  $\Delta H$  and  $T_g$  all decrease with the increasing of MDR, but the trend becomes unnoticeable in the middle and final stage (unshown in this report).

In order to corroborate the above results and find which one has the main effect on the physical aging, a series of experiments were performed on the samples achieved on different circumstances (Table 2 shows the samples and corresponding conditions). The aging results are shown in Fig. 6 in which a part of the values is taken from Table 2. The results have the consistency that when the amorphous samples were stretched at higher speed and up to higher ratio, which would inevitably give rise to increased  $\Delta n$ , the  $\Delta H$  became lower and the  $T_g$  became unobvious. Apparently, the development of physical aging is 'interrupted' by escalating orientation. These results come from the decrease of the available amorphous phase which undergoes relaxation as the ordered phase of the material increases<sup>[6]</sup>.

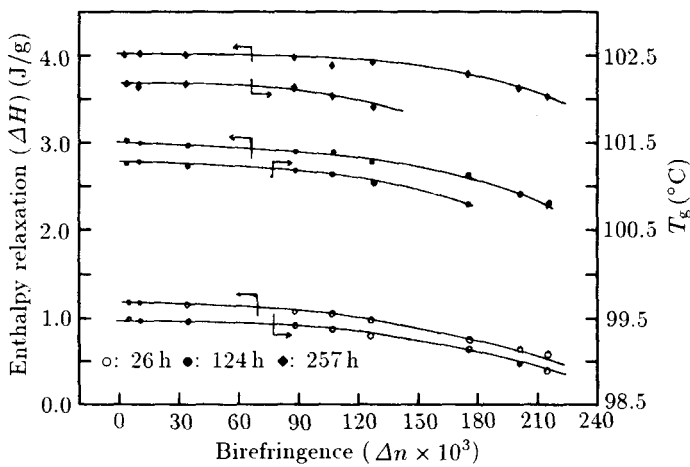


Fig. 5 Enthalpy relaxation  $\Delta H$  vs .  $\Delta n$  for aPS samples aged for three selected times

**Table 2** Preparation of aPS samples at different drawing speeds and draw ratios  
(all films are drawn at temperature 120°C)

| Draw ratio (DR)*    | MDR  | $\Delta n(\times 10^3)$ | Density (g·cm <sup>-3</sup> ) |
|---------------------|------|-------------------------|-------------------------------|
| 1.10                | 1.02 | 110.2                   | 1.0474                        |
| 1.18                | 1.06 | 100.8                   | 1.0472                        |
| 1.22                | 1.08 | 94.4                    | 1.0472                        |
| 1.37                | 1.12 | 82.9                    | 1.0476                        |
| 1.47                | 1.23 | 78.1                    | 1.0477                        |
| 1.59                | 1.30 | 70.5                    | 1.0471                        |
| 1.82                | 1.47 | 62.6                    | 1.0469                        |
| 1.96                | 1.49 | 43.0                    | 1.0468                        |
| 2.04                | 1.26 | 32.3                    | 1.0470                        |
| 2.56                | 1.28 | 24.4                    | 1.0471                        |
| Draw speed (/min)** | MDR  | $\Delta n(\times 10^3)$ | Density (g·cm <sup>-3</sup> ) |
| 0.21                | 1.03 | 19.6                    | 1.0476                        |
| 0.35                | 1.08 | 22.7                    | 1.0477                        |
| 0.47                | 1.14 | 45.2                    | 1.0472                        |
| 0.59                | 1.21 | 57.6                    | 1.0470                        |
| 0.74                | 1.26 | 96.4                    | 1.0477                        |
| 0.96                | 1.33 | 120.5                   | 1.0479                        |
| 1.23                | 1.37 | 131.2                   | 1.0472                        |
| 1.50                | 1.42 | 162.0                   | 1.0473                        |
| 1.78                | 1.44 | 177.1                   | 1.0478                        |

\* Draw speed =0.21/min; \*\* Draw ratio =1.22

Drawing, even at temperatures above  $T_g$ , will inevitably introduce the alignment of chains, so the samples studied are not in the isotropic state which generally is the essential state of physical aging of amorphous glassy polymers, but it is relatively reasonable to assume that the physical aging can evolve in this formed unisotropic state.

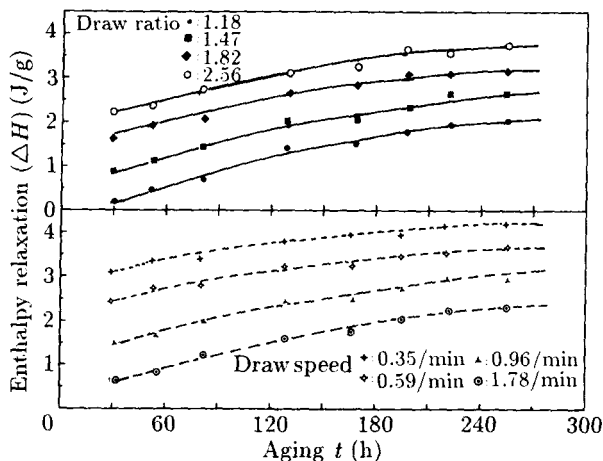


Fig. 6. Variation of  $\Delta H$  vs. aging time for samples achieved under different drawing conditions

Until now, on the study of physical aging, there are several theories and models have been put forward in an attempt to shed more light on this area of research<sup>[7]</sup>. As to the decrease of  $\Delta H$  and  $T_g$  with increasing of  $\Delta n$ , this could be tentatively interpreted with the viewpoint of cohesive entanglement. As Qian termed<sup>[8]</sup>, the 'cohesive entanglement' is the local alignment of neighboring chain segments originated from inter-chain cohesion. As topological entanglement, the new kind of entanglement can also serve as physical crosslinks to form a temporary network. So it became understandable that the alignment caused by drawing would profoundly hinder the development of entanglement points.

However, it should be made clear that the data presented here do not provide direct evidence for this speculation. Further studies in our laboratory are under way currently on some other polymers such as polycarbonate (PC) and polymethyl methacrylate (PMMA), in order to verify ultimately whether orientation in the local sense or/global sense should play an unfavorable effect on the physical aging.

## CONCLUSION

Relaxation enthalpy ( $\Delta H$ ) and  $T_g$ , which can act as the criterion of physical aging

in the d.s.c. tests, have variant dependence on the molecular draw ratio (MDR) and optical birefringence ( $\Delta n$ ) which can be treated as the degree of extension and orientation of segment, respectively. M d.s.c. results show that the local segmental orientation would retard the evolution of physical aging; the molecular orientation presents an unfavorable effect on the development of physical aging in the amorphous region of atactic PS especially in the early stage of the process, but when the samples are strained up to high extent, the drawing effect on the successive aging will become undetectable.

**Acknowledgements** We wish to thank Professor D.Y. Shen for the provision of laboratory facilities and for his encouragement during this work.

### REFERENCES

- [1] Qian, R.Y., Shen, D.Y., Sun, F.G., *Macromol. Chem. Phys.*, **1996**, 197, 1485
- [2] Reading, M., *Trends Polym. Sci.*, **1993**, 1 (8), 248
- [3] Hinrichsen, G., Adam, H.G., Krebs, H., *Colloid & Polymer Sci.*, **1980**, 258, 232
- [4] Porter, R.S., Wang, L.H., *J. Macromol. Sci. —Rev. Macromol. Chem. Phys.*, **1995**, C35 (1), 61
- [5] Ajji, A., Guevremont, J., Dumoulin, M.M., *Polymer*, **1996**, 37 (16), 3707
- [6] Tsitsillianis, C., Bokaris, E.P., *Polymer Bulletin*, **1993**, 30, 609
- [7] Song, R., Fan, Q.R., *Polymer Bulletin* (in Chinese), **1997**, (4), 226
- [8] Qian, R.Y., Wu, L., Napper, D.H., *Macromolecules*, **1993**, 26, 2950
- [9] Tant, M.R., Wilkes, G.L., *J. Appl. Polym. Sci.*, **1981**, 26, 2813
- [10] Tsitsilians, C., Tsapatsis, M., Economou, Ch., *Polymer*, **1989**, 60, 1861