Polymer Bulletin 47, 91–97 (2001)

Polymer Bulletin

Amorphous phase in atactic polystyrene

Jun Zhao, Qingrong Fan (✉)

State Key Laboratory of Polymer Physics & Chemistry, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China
e-mail: qrfan@pplas.icas.ac.cn, Tel.: +86-10-62563065, Fax: +86-10-62559373

Received: 10 July 2001/Accepted: 24 July 2001

Summary

Amorphous phase in atactic polystyrene (a-PS) was investigated via its physical aging behavior. It was found that when the samples were quenched rapidly, there were dual amorphous regions with quite different characters: free amorphous region and constrained amorphous region. The former was the normal bulk amorphous region, while the latter was constrained by the internal stress. The dual amorphous regions exhibited as dual endothermic peaks in differential scanning calorimetry (DSC) traces when the samples were physically aged at temperatures well below the glass transition temperature (T_g). The lower peak corresponded to the free amorphous region, and the upper peak to the constrained amorphous region.

Introduction

Physical aging in amorphous polymers refers to the change of properties such as specific volume, enthalpy, and entropy, as a function of storage time [1]. It occurs only when the temperature is below the glass transition temperature (T_g). Physical aging also occurs in the amorphous phase of semicrystalline polymers [2-4]. Thus, characters of amorphous phase can be obtained by studying its physical aging behavior. As a matter of fact, physical aging has proved to enhance the thermal response at the glass transition of polymers [5]. Therefore, more details can be obtained about the structural change in amorphous phase.

In early years, physical aging was experimentally studied mainly by measuring volume relaxation of the samples via dilatometry [6], but later more studies were about enthalpy relaxation via calorimetry which was convenient, sensitive, and highly reproducible [7-9]. One of the earlier studies by Petrie established the equivalence between the energy absorbed during the heating run through the glass transition region and the enthalpy lost during the physical aging [7].

It was Illers et al. that first observed the dual endothermic peaks appearing in differential scanning calorimetry (DSC) traces of poly(vinyl chloride) (PVC) quenched rapidly and then physically aged [10]. Ruddy et al. found that the dual peaks could be observed only when the amorphous polymers were quenched rapidly and then heated slowly [11]. Shultz et al. observed that the lower peak shifted to higher temperature with increasing physical aging temperature (T_{pa}) and time (t_{pa}) [12]. Hodge et al. reported that it was the intensity of the lower peak but not its peak temperature that highly depended upon the previous thermal history [13]. Recently, Hourston et al. pointed out that the lower peak appeared only when the T_{pa} was well below the T_g [14].

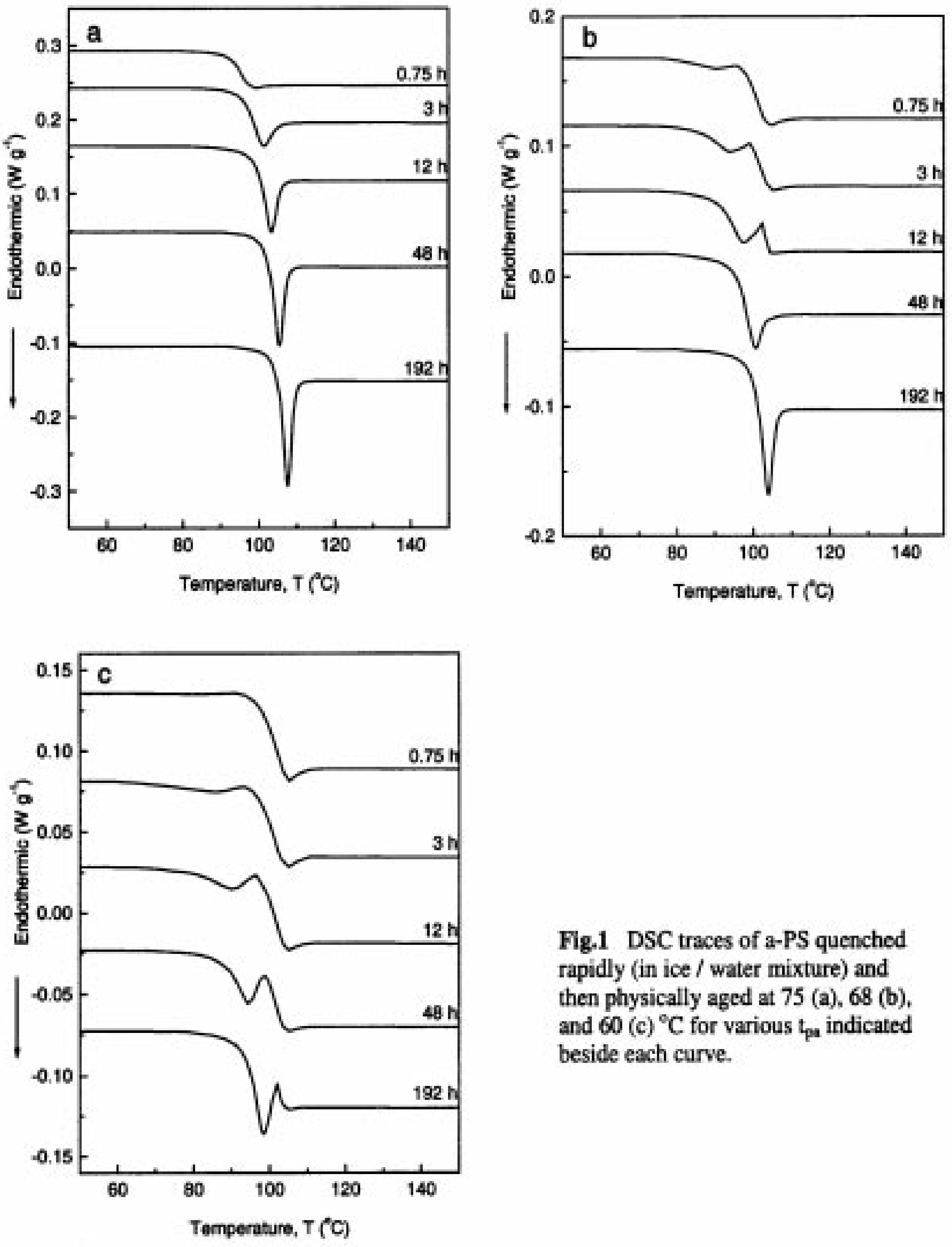

Fig.1 DSC traces of a-PS quenched rapidly (in ice / water mixture) and then physically aged at 75 (a), 68 (b), and 60 (c) °C for various t_{pa} indicated beside each curve.

With respect to the physical nature of the dual endothermic peaks, different researchers reached different conclusions from their own experimental results. The upper peak was regarded as the normal physical aging peak by almost all the researchers, while the lower peak was ever attributed to the distribution of relaxation times, β relaxation, and phase separation [11-16].

Recently, Li et al. found that appearance of the dual endothermic peaks in DSC traces of thermoset epoxy resin could be attributed to the internal stress which resulted from the rapid quench [17-20]. In this paper, our systematic investigations on atactic polystyrene (a-PS) will prove that this explanation is also suitable for thermoplastic polymers. A concept of dual amorphous regions will also be put forward.

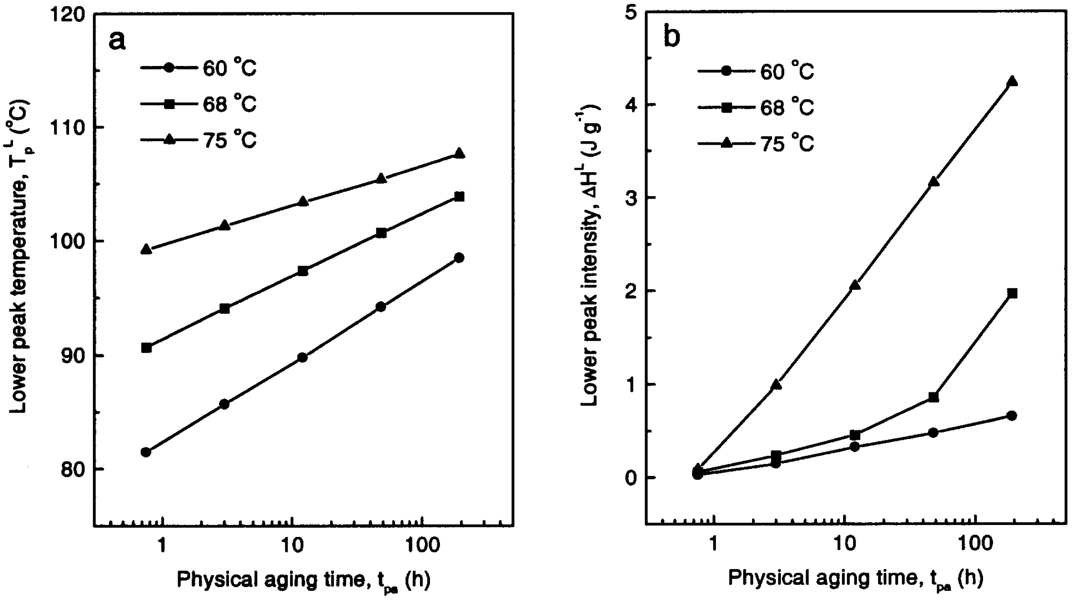

Fig. 2 Evolution of T_p^L (a) and ΔH^L (b) with increasing t_{pa} for a-PS quenched rapidly (in ice / water mixture) and then physically aged at various T_{pa} indicated in the corner (calculated from Figure 1).

Experimental

Samples preparation

a-PS pellets were kindly supplied by Jiamusi Synthetic Material Company Ltd., Heilongjiang Province. They had a viscosity-average molecular weight of ca. 1.5 x 10^5. As-received samples were hot-pressed at ca. 200 °C to prepare films with a thickness of ca. 160 μm.

Thermal treatments

The prepared a-PS films were cut into equal circles with a diameter of ca. 5.7 mm. They were held in an oven in nitrogen atmosphere at 180 ± 0.5 °C for 5 min to completely eliminate previous thermal history. Then they were quenched rapidly in ice / water mixture or cooled slowly at 5 °C min^{-1} in the oven. Subsequently, the quenched samples were physically aged in an oven in nitrogen atmosphere at various temperatures for predetermined periods of time before DSC measurements.

DSC measurements

Physically aged samples of ca. 4.5 mg were sealed in aluminum pans, and their thermal properties were measured by using a TA2910 DSC. Indium and tin were employed for the temperature calibration, the heat capacity was evaluated with respect to sapphire as a standard, and a nitrogen gas purge with a flux of ca. 30 mL min^{-1} was used to prevent oxidative degradation of samples during the heating run. The rate of heating run was 10 °C min^{-1}. A heating run of the unaged samples was pre-performed. So the peak intensity of the physically aged samples could be calculated by the discrepancy between their traces and that of the unaged samples.

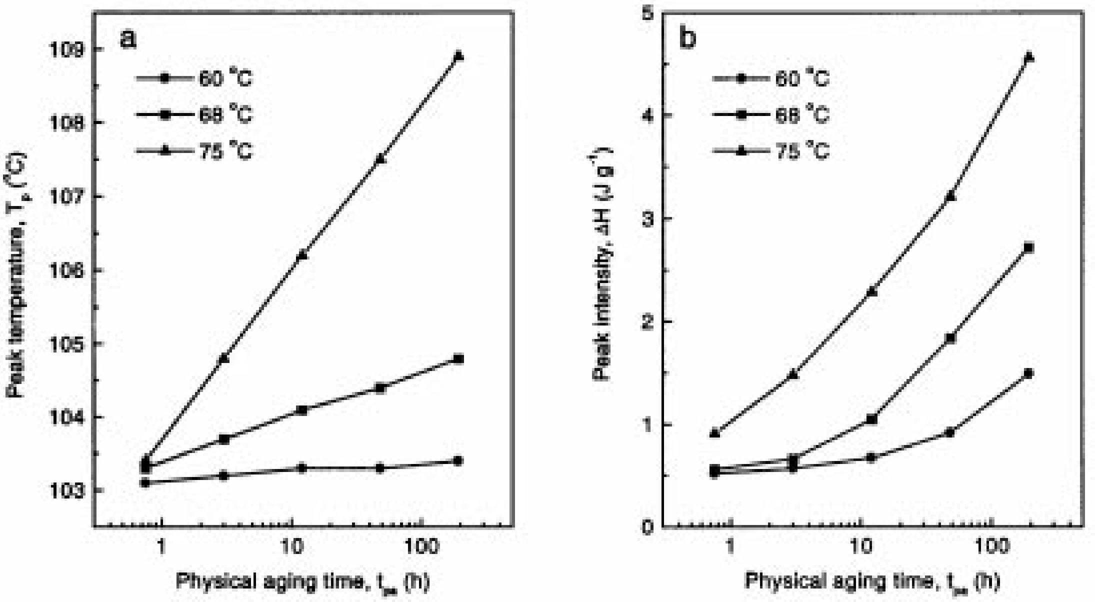

Fig. 3 Evolution of T_p (a) and ΔH (b) with increasing t_{pa} for a-PS cooled slowly (at 5 °C min^{-1}) and then physically aged at different T_{pa} indicated in the corner.

Results and discussion

Figure 1a presents DSC traces of a-PS quenched rapidly and then physically aged at 75 °C. It can be seen that there was only a single endothermic peak appearing in the Tg region. The peak shifted to higher temperature and its intensity also increased with increasing t_{pa}. These experimental results are well known and consistent with many others' research on a-PS, poly(ethylene terephthalate) (PET), and other polymers [7-9].

Figure 1c presents DSC traces of a-PS quenched rapidly and then physically aged at 60 °C. Dual endothermic peaks could be observed. The upper peak appeared in the T_g region, while the lower one in the temperature region well below the T_g. With the proceeding of physical aging, the lower peak shifted to higher temperature with increasing intensity, while the upper one kept at almost the same temperature with decreasing intensity.

Figure 1b presents DSC traces of a-PS quenched rapidly and then physically aged at 68 °C, which is between the T_{pa} shown in Figures 1a and 1c. Dual endothermic peaks could be seen at the beginning of the physical aging. After a t_{pa} of 48 h, however, there was only a single endothermic peak. According to the evolution laws, it can be easily found that the single peak was the lower peak but not the upper peak. Correspondingly, the single peak for the T_{pa} of 75 °C had the same physical nature as the lower peak but not the upper peak.

For the T_{pa} above 75 °C, the physical aging behavior was similar to that at 75 °C, and for the T_{pa} below 60 °C, the physical aging behavior was similar to that at 60 °C. That is to say, low enough T_{pa} was necessary for the appearance of the dual peaks and the upper peak.

Our experiments showed that cooling medium was also an important factor in determining the appearance of the dual peaks and the upper peak. The cooling medium in Figure 1 was ice / water mixture, where the cooling rate was fairly high. When liquid nitrogen with a higher cooling rate was used as the cooling medium, the dual endothermic peaks could also be observed. But when air with a cooling rate lower than ice / water mixture was used as the cooling medium, no dual peaks could be found. Therefore, cooling medium with a high enough cooling rate was also necessary for the appearance of the dual peaks and the upper peak.

According to the experimental results shown above, it seems reasonable to assume that it was the internal stress produced during the rapid quench that determined the appearance of the dual peaks and the upper peak [17-20]. As a matter of fact, it is inevitable that some internal stress were frozen-in when the polymers were quenched rapidly from temperatures above the T_g to below the T_g. It has been reported that increasing internal stress caused increasing T_g, which means that the internal stress constrained the mobility of the molecular segments [21].

From this viewpoint, a concept of dual amorphous regions can be put forward. It has been well accepted that there were dual and even multiple amorphous regions in semicrystalline polymers due to the different constraint that the crystallites played on them [1,3]. It seems reasonable to assume that there were also dual and even multiple amorphous regions in rapidly quenched a-PS due to the different constraint that the frozen-in internal stress played on them. The internal stress increased with increasing cooling rate, so did the constraint that the internal stress played on the amorphous region. The different internal stress produced different amorphous regions: free amorphous region with low or even no internal stress and constrained amorphous region with high internal stress. Of course, this is a simplified way to divide the amorphous phase of rapidly quenched amorphous polymers. To speak strictly, there was a distribution of amorphous regions according to the different constraint that the internal stress played on them. The internal stress relaxed gradually coupled with the enthalpy and volume relaxation during the physical aging. And with the relaxation of the internal stress, constrained amorphous phase changed into the free amorphous phase.

When the concept of dual amorphous regions has been established, all our experimental results can be explained successfully. For the rapidly quenched samples, there were different internal stress and correspondingly different amorphous regions: free amorphous region without internal stress and constrained amorphous region with internal stress. Thus, for the T_{pa} of 60 °C well below the T_g, dual endothermic peaks appeared corresponding to the physical aging of the dual amorphous regions: the lower peak corresponded to the free amorphous region and the upper peak to the constrained amorphous region. With the proceeding of physical aging, internal stress relaxed gradually, so increasing amount of the constrained amorphous region changed into the free amorphous region. Therefore, the intensity of the upper peak decreased and its peak temperature kept almost unchanged, although the extent of the physical aging increased with increasing t_{pa}. The lower peak shifted to higher temperature with increasing intensity due to not only the increasing extent of the physical aging but also the increasing amount of the free amorphous region. For the T_{pa} of 75 °C below but close to the T_g, the constrained amorphous region changed into the free amorphous region so rapidly that the constrained free amorphous region disappeared after a very short t_{pa}. Thus, only the lower peak appeared in the DSC traces, which shifted to higher temperature with increasing intensity due to the increasing extent of physical aging. For the T_{pa}, of 68 °C between the two cases mentioned above, the constrained amorphous region changed into the free amorphous region at a moderate rate. Therefore, the disappearance process of the upper peak with increasing t_{pa} could be seen clearly. The lower peak shifted to higher temperatures with increasing intensity similar to that for T_{pa} of 60 and 75 °C.

Figure 2 presents the comparison between the evolution laws of the lower peak for T_{pa} of 60 and 68 °C and the single peak for T_{pa} of 75 °C. It can be seen that they had the similar evolution laws, which means that they had the same physical nature. The peak temperature of the lower peak (T_p^L) increased with increasing T_{pa} and so did the peak intensity (ΔH^L). These results were due to the increasing rate of enthalpy relaxation with increasing T_{pa}.

As for the physical aging behavior of the samples cooled slowly, there was only the free amorphous region because the internal stress had been relaxed during the slow cooling. Therefore, there was only a single endothermic peak shifting to higher temperature with increasing intensity. The endothermic peak of the samples cooled slowly and then physically aged had the same physical nature as the lower peak discussed above. For the same physical aging condition (the same T_{pa} and t_{pa}), the endothermic peak of the slowly cooled samples appeared at higher temperature with higher intensity than the lower peak of the rapidly quenched samples due to the additional physical aging occurred during the slow cooling (See Figure 3).

In conclusion, our experimental results showed that there were dual amorphous regions in rapidly quenched a-PS due to the different internal stress: free amorphous region and constrained amorphous region. They exhibited as the dual endothermic peaks in DSC traces when the samples were physically aged at temperatures well below the T_g.

Acknowledgements.

This work was subsidized by the Special Funds for Major State Basic Research Projects (95-12 and G1999064800).

References

1. Hutchinson JM (1995) Prog Polym Sci 20:703.
2. Schael GW (1966) J Appl Polym Sci 10:901.
3. Struik LCE (1989) Polymer 30:815.
4. Zhao J, Song R, Zhang Z, Linghu X, Zheng Z, Fan Q (2001) Macromolecules 34:343.
5. Vigier G, Tatibouet J, Benatmane A, Vassoille R (1992) Colloid Polym Sci 270:1182.
6. Hutchinson JM, Kovacs AJ (1976) J Polym Sci Polym Phys 14:1575.
7. Petrie SEB (1972) J Polym Sci A-2(10):1255.
8. Hutchinson JM, Smith S, Home B, Gourlay GM (1999) Macromolecules 32:5046.
9. Song R, Zhao J, Yang J, Linghu X, Fan Q (2001) Macromol Chem Phys 202:512.
10. Illers KH (1969) Makromol Chem 127: 1.
11. Ruddy M, Hutchinson JM (1988) Polym Commu 29:132.
12. Shultz AR, Young AL (1980) Macromolecules 13:663.
13. Hodge IM, Berens AR (1982) Macromolecules 15:762.
14. Hourston DJ, Song M, Hammiche A, Pollock HM, Reading M (1996) Polymer 37:243.
15. Kreibich UT, Schmid R (1975) J Polym Sci Symposium 53:177.
16. Montserrat S (1994) J Polym Sci Polym Phys 32:509.
17. Wang H, Li S, Ye J (1992) J Appl Polym Sci 44:789.
18. Wang H, Li S, Yu T (1993) Polym Eng Sci 33:1027.
19. Li S, Shen J, Chen X, Chen R, Luo X (1997) J Macromol Sci Phys B36(3):357.
20. Chen X, Li S (1998) Polym Eng Sci 38:947.
21. Brahatheeswaran C, Gupta VB (1993) Polymer 34:289.