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Enthalpy relaxation studies in isotactic polystyrene. Effects of crystallinity

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SUMMARY.

The enthalpy relaxation of the amorphus isotactic polystyrene is strongly affected from the crystalline phase induced by annealing at temperatures between T_g and T_m. All the parameters describing the relaxation process, $\Delta\Delta H$, T_{max} and T_{ons} depend also on the above T_g annealing conditions as the induced crystallinity alters the quantity and the quality (i.e.T_g,T_{gons},ΔT_g) of the remaining amorphous phase.

INTRODUCTION

It is well established that polymer glasses undergo relaxation processes arising from their nonequilibrium glassy state (1-7). The main thermodynamic parameters which change with time are the volume and the enthalpy provoking changes in many physical properties of the polymer, e.g. mechanical (8) or transport properties (9).

During the last years the study of the enthalpy relaxation of the glassy polymers has been focused also on the investigation of phase phenomena in polymer blends (10-14) as well as in block copolymers (15,16). The practice imposes careful examination of all the factors which could affect the relaxation parameters e.g. the enthalpy relaxation, ΔH, the onset T_{ons}, and the maximum, T_{max}, of the enthalpy relaxation peak. These parameters are known to depend on the cooling rate q_1 when the sample is cooled from temperatures above T_g to temperatures T_A below T_g, the annealing temperature T_A, the annealing time t_A and the heating rate q_2 when the sample is reheated to reach the equilibrium state.

Another factor that affects the relaxation parameters is the crystallinity which can be induced when the polymer sample is kept at temperatures above T_g as it has been demonstrated for poly(vinyl chloride) (PVC) recently (17). As it has been shown the enthalpy relaxation of PVC induced by sub-T_g annealing strongly depends on the above-T_g annealing conditins e.g. the crystallization temperature T_c and the time t_c which finally are responsible for the state of the remaining amorphous phase.

In this communication the enthalpy relaxation of isotactic polystyrene (iPS) which shows a different crystallinity behaviour of PVC will be presented. It is known that the iPS forms an amorphous glassy phase when it is rapidly quenched from the melt to temperatures below the glass transition temperature. The aim of this study is to investigate the influence of the crystallinity on the relaxation behaviour of the remaining amorphous iPS phase and how all these parameters describing the relaxation process are affected by the induced crystallinity.

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EXPERIMENTAL

The iPS sample was prepared by polymerizing styrene in hexane at 70°C using $TiCl_3$-$(C_2H_5)_3Al$ as catalyst. The polymer obtained was purified in boiling methyl ethyl ketone (MEK) to extract the remaining atactic material. The molecular weight has been determined by viscometry in Cl-benzene at 25°C according to the procedure of Utiyama. Its M_v=2,800,000 g/mol.

DSC measurements were performed in a Du Pont 910 calorimeter equipped with a 99 thermal analyser. The instrument was calibrated with an indium standard. The heating rate was 20°C/min.

The enthalpy relaxation ΔH was estimated from DSC thermograms measuring the area enclosed between the traces of the sub-T_g annealed and quenched samples. T_{ons} of the enthalpy relaxation peak is defined as the intersection point between the extrapolated baseline established below T_g and the tangent drawn on the low temperature side of the endothermic peak on T_g area.

RESULTS AND DISCUSSION

All the samples were pre-heated at 245°C for 15 min, a temperature higher than the melting temperature, T_m, of the crystalline phase of the iPS, to assure identical thermal histories. In the following the samples were crystallized at temperatures (T_c) between the T_g and T_m for a given time t_c and quenched to 0°C. The samples having different crystallinity portions were then subjected to annealing at temperatures T_A below T_g for a given period of time t_A, quenched to 0°C and scanned in the DSC at a rate of 20°C/min. The above thermal history can be described according to the scheme

$$245^{\circ}C(15\ min) \rightarrow T_c(t_c) \rightarrow 0^{\circ}C \nearrow T_A(t_A) \rightarrow 0^{\circ}C$$

A typical thermogram of a sample with the above thermal history is illustrated in figure 1. Two points have attracted our attention: the endotherm in T_g area corresponding to the enthalpy relaxation of the amorphous phase and the endotherm (230°C) corresponding to the melting of the crystalline phase of the material.

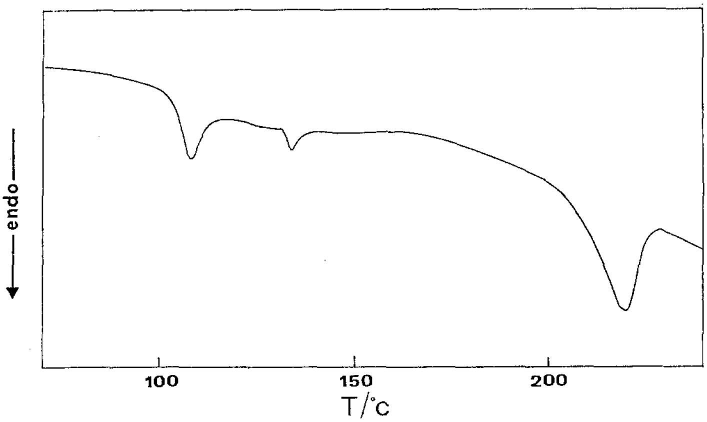

Fig.1. DSC thermograms of iPS crystallized at 132°C (24h) and annealed at 82°C for 24h.

This thermal treatment allows us to investigate the relaxation behaviour of the amorphous phase when different crystallinity percentage have been induced in the material. In figure 2 the enthalpy relaxation, ΔH, of the amorphous iPS annealed at 80°C is given as a function of the logarithm of the annealing time, tA, for three different kinds of samples. The first was quenched from the melt, the second was crystallized at 130°C for 24h and the third was used without any thermal treatment. The crystallinity of these samples increases in the order: quenched < crystallized at 130°C < un-treated.

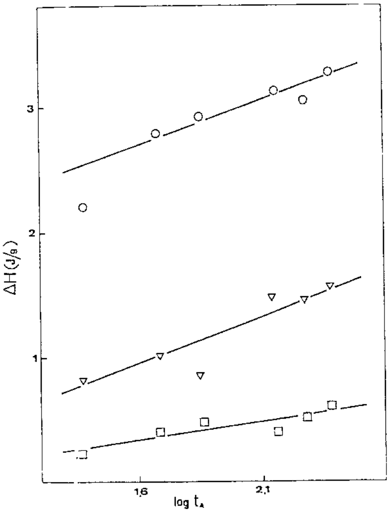

Fig.2

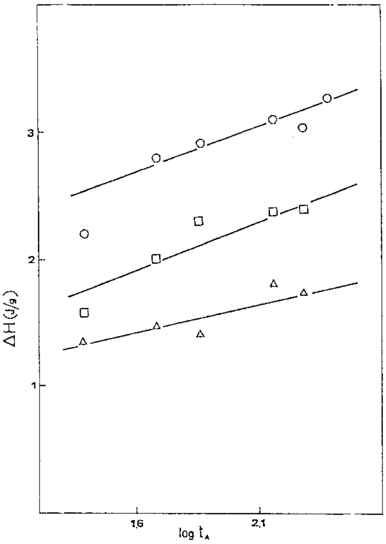

Fig.3

Fig.2. Enthalpy relaxation ΔH as a function of logtA for iPS : (○) quenched from the melt. (▽) crystallized at 130°C (24h) (□) as received.

Fig.3. Enthalpy relaxation ΔH as a function of logtA for iPS : (○) quenched from the melt, (□) crystallized at 207°C (10min) (△) Crystallized at 207°C (45min).

As it is shown the enthalpy relaxation decreases with increasing degree of crystallinity. These results are due to the decrease of the available amorphous phase which undergoes relaxation as the crystalline phase of the material increases. It seems clearly that the immobilization of the segments bound in the crystallites is the reason for the reduction of the enthalpy relaxation. Another experiment also was performed in order to corroborate the above result. Samples crystallized at 207°C for 10 and 45 min were subsequently annealed at 80°C for different annealing times. The enthalpy relaxation ΔH as a function of the logarithm of the annealing time, tA, is depicted in figure 3. For comparison the curve for the quenched sample is also presented in the figure. Again one can observe a shift of the ΔH versus logtA curves towards lower values as the crystallization time tc increases. Theese results are in accordance with those presented in figure 2.

Besides the magnitude of the enthalpy relaxation other important parameters concerning the position of the enthalpy relaxation peak as it is the maximum

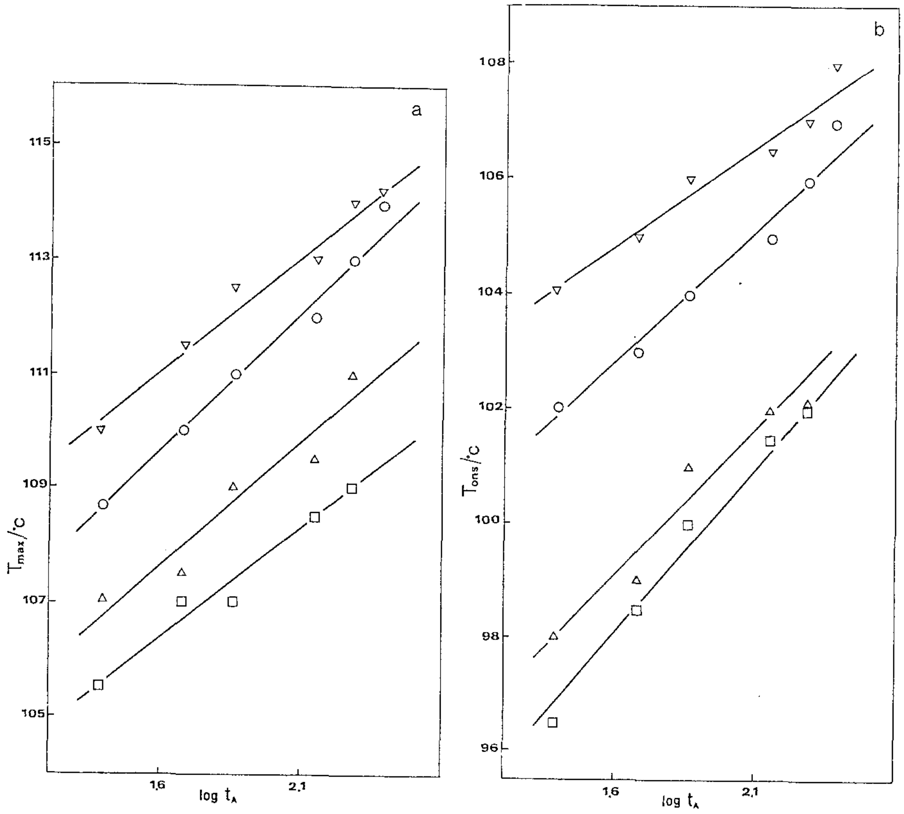

Fig.4. Tmax (a) and Tons (b) as a function of logtA for iPS : (▽) crystallized at 130°C (24h), (○) quenched from the melt, (△) crystallized at 207°C (45min), (□) crystallized at 207°C (10min).

Table 1 : Glass transition temperature of iPS with different thermal histories

thermal history	$T_{g\ ons}$(°C)	T_g(°C)	ΔT_g(°C)
quenched from the melt	97	101	9
annealed 130 °C (24h)	94	102	15
annealed 207 °C (10min)	90	96	12
annealed 207 °C (45min)	92	97	10

T_{max} and the onset T_{ons} of this peak have to be investigated.

These two parameters are mainly used for the investigation of the polymer miscibility in polymer blends (10,11,13) and copolymers (15,16). Therefore the inspection of possible differentiations with respect to the induced crystallinity is of increasing interest.

It is known that T_{max} and T_{ons} are governed by many factors as are the annealing temperature T_A, the annealing time t_A, the T_g of the polymer, the width of the glass transition temperature, some other structural parameters as they are the characteristic relaxation times of the material as well as the heating rate on the DSC experiment.

Figure 4 shows T_{max} and T_{ons} as a function of $logt_A$ for the various iPS samples with different crystallinity which has been induced under different conditions. Both T_{max} and T_{ons} show approximately a linearly dependence on $logt_A$ a typicall behavior for the glassy amorphous polymers when they are not very close to equilibrium. Considerable differences are observed for T_{max} between samples with different crystallinity.They are more pronounced on T_{ons}.

More precisely the curve for the iPS annealed at 130°C (24h) lies above the curve corresponding to the quenched sample while the curves for the samples annealed at 207°C for 10 and 45 min lie below the curve of the quenched sample. Keeping constant all the parameters that could affect the position of the maximum of the peak e.g. T_A, heating rate, cooling rate etc., the interpretation of the above results have to be inquired on the induced crystallinity. The diminution of the amorphous phase due to the induced crystallinity should not provoke any differentiation of the position of the peaks. Consequently possible differences of T_g of the remaining amorphous phase have to be examined. Three parameters concerning the glassy state of the polymer are considered : The onset of the glass transition region, T_{gons}, which is defined as the intersection between the extrapolated baseline before T_g and the line drawn through the point of inflection of the incremental change in C_P, the T_g of the half C_P change and ΔT_g,the width of the glass transition region, which is the difference between T_{gons} and the temperature of the intersection of the extrapolated baseline above T_g and the line drawn through the point of inflection of the incremental change in C_P. All these parameters are summarized in table I for the various crystallized iPS samples.

The most significant differences observed in T_{max} and T_{ons} are those between the samples crystallized at 130°C (24h) and 207°C (45min). The shift of the curve of T_{max} or T_{ons} corresponding to the former samples about 5°C or 6°C towards higher temperatures with respect to the later can be attributed mainly to higher values of T_g and T_{gons} by 4 and 6°C respectively. Generally one can observe that the higher T_g or T_{gons} the higher the T_{max} or T_{ons} of the enthalpy relaxation peaks.

The only disagreement with the above observation is that the T_{ons} of the sample annealed at 130°C is higher than that of the quenched sample despite its T_{gons} is lower. This could be attributed to the broadening of the T_g region of the annealed sample towards higher temperatures ($\Delta T_g = 15$°C).

The observed differences in T_g and therefore in the enthalpy relaxation parameters of these semicrystalline polymer samples could be interpreted considering the Struik model (8). According to that model in the vicinity of the crystalline regions there exist some regions of reduced segmental mobility, the so called disturbed regions, which provoke a shift of the Tg area. The extention and the state of these disturbed regions depend on the state of the crystalline phase, e.g. the extension and the quality of the crystallites (17). Therefore the above-Tg annealing conditions (e.g. Tc, tc) affect the Tg of the material and consequently the relaxation process of the glassy state towards equilibrium.

In the following samples were isothermally crystallized at different Tc between 130 and 210°C for 1h and subsequently annealed at 82°C for 120h according to the scheme presented previously. The enthalpy relaxation of these samples as a function of the heat of melting of the crystallites (ΔHm), reflecting the degree of crystallization, is presented in figure 5. ΔHm has been calculated from the total area of all the endothermic peaks appearing on DSC thermograms. At temperatures between 140 and 195°C three melting peaks are evidenced in accordance with the results of Lemstra et al. (19). The peak of the lowest Tm originates from secondary crystallization process between the lamellaes and is incorporated on the calculation of ΔHm.

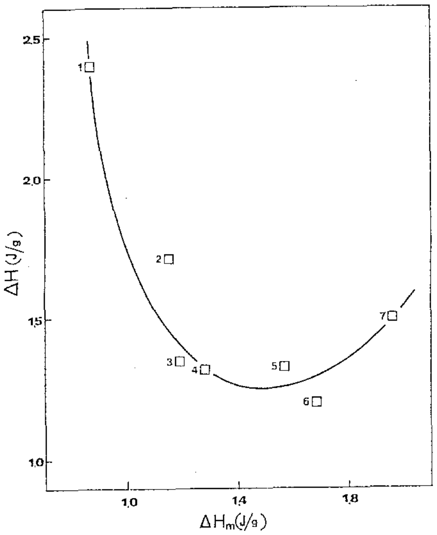

Fig 5

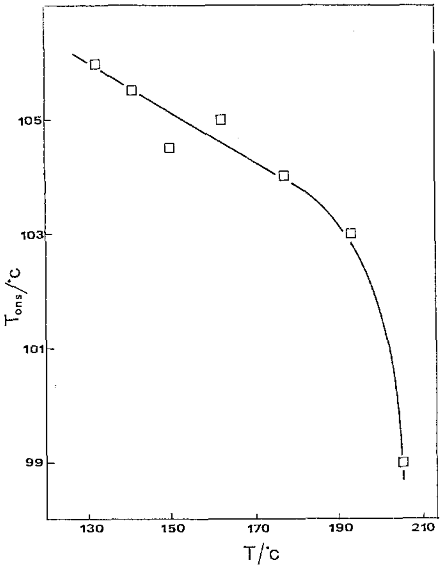

Fig 6

Fig.5. Enthalpy relaxation ΔH as a function of the enthalpy of fusion ΔHm for iPS crystallized for 1h at different temperatures : (1) 132°C, (2) 141°C, (3) 162°C, (4) 151°C, (5) 193°C, (6) 177°C, (7) 205°C.

Fig.6. Tons as a function of the crystallization temperature.

Figure 5 shows an upward curvature at high values of ΔHm. What one could expect is a monotonous decrease of the enthalpy relaxation as the crystallinity increases. In Figure 6 the Tons of the enthalpy relaxation peak is given as a function of the crystallization temperature Tc.

The observed abrupt decrease of the Tons at Tc=207°C is in agreement with the results already mentioned and can explain the behaviour resulted from figure

5. In fact the decrease of T_{ons} has been attributed to the lowering on T_{gons} (table I) which causes a decrease in the difference T_g-T_A and therefore an increase of ΔH.

It could be concluded that the influence of the crystallinity, which has been induced at different above-T_g annealing conditions, on the enthalpy relaxation phenomena is more complicated than expected as the remaining amorphous phase is differentiated and is affected from the state of the induced crystallinity.

CONCLUSIONS

The enthalpy relaxation of iPS and the influence of crystallinity induced by annealing at temperatures between T_g and T_m has been studied. All the parameters describing the relaxation process of the amorphous phase, e.g. ΔH, T_{max} and T_{ons} are affected by the presence of the crystalline phase. In general the changes of these parameters depend upon the above-T_g annealing conditions which are responsible for the state of the remaining amorphous phase. As it is observed the amorphous phase is altered quantitatively and qualitatively

A practical consequence of this study is that samples of semicrystalline polymers for which enthalpy relaxation studies are demanded have to be pre-heated at temperatures well above T_m before any sub-T_g annealing experiment is performed. Special care has to be taken into account in the case of polymer miscibility investigation. Small defferentiations in T_{max} or T_{ons} of the relaxation peaks of the blend components arising from possible crystallization could lead in erroneous conclusions.

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