Differential scanning calorimetric studies on the glass transition temperature of polyhydroxystyrene derivatives containing sorbed water

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Poly(4-acetoxystyrene) (PAS) and poly(4-acetoxy-3-methoxystyrene) (PAMS), poly(4-hydroxystyrene) (PHS) and poly(4-hydroxy-3-methoxystyrene) (PHMS) have been prepared. The effects of hydrogen bonding on the glass transition temperatures (T_g) of these polymers have been studied by differential scanning calorimetry. The T_g's of partially hydrolyzed PAS and PAMS increased with the degree of hydrolysis. Partially hydrolyzed PAS and PAMS are estimated to be random copolymers, judging from the correspondence between the calculated and observed T_g's of these polymers. The effect of water on the glass transition was also studied, and it was clarified how water adsorbed on the polymers acts as a hydrogen-bond breaker. The 'critical water content' is calculated from the decrease of T_g by water absorption, and the relation between hydrogen bonding and T_g is discussed.

INTRODUCTION

In its thermal properties lignin, the second most abundant component in higher plants, has several unique characteristics[1]. Lignin molecules consist of different basic units[2] joined to each other mainly by hydrogen bonds. Accordingly, the effect of the hydroxyl groups on the thermal properties of lignin and lignin-related compounds are of interest in connection with the question of the nature of hydrogen bonding.

In the previous paper[3], we reported the thermal properties of the styrene derivatives, poly(4-hydroxystyrene)(PHS) and poly(4-hydroxy-3-methoxystyrene)(PHMS), whose substituent groups are related to the 4-hydroxyphenyl and guaiacyl groups in lignin. These styrene derivatives have been proved to be biodegradable[4] and also have some advantageous mechanical properties, especially high strength compared with that of polystyrene[5,6]. Moreover, the glass transition temperatures (T_g) of these styrene derivatives are $\sim$20–80°C higher than those of polystyrenes[3]. These facts have been attributed to the hydrogen bonds formed between hydroxyl groups in the substituents of these styrene derivatives.

In this paper we report results from differential scanning calorimetry (d.s.c.) to demonstrate semiquantitatively the effects of hydrogen bonding on the thermal properties of PHS, PHMS, poly(4-acetoxystyrene) (PAS), poly(4-acetoxy-3-methoxystyrene' (PAMS) and partially hydrolyzed PAS and PAMS. The effect of water on the T_g's of PAS, PAMS and hydrolyzed PAS and PAMS is also considered.

EXPERIMENTAL

Samples

PHS, PAS, PHMS and PAMS (*Figure 1*) were synthesized by the procedure reported previously[3-5].

Polymers with acetoxyl groups were hydrolyzed as follows: PAS (PAMS) (1 g) was dissolved in 100 ml of acetone, and concentrated hydrochloric acid (2 ml) was stirred into this solution. The mixture was allowed to stand for various time intervals (1–24 h) at temperatures from 45 to 65°C. The resulting mixture was stirred slowly into large amounts of ice cold water, filtered, repeatedly washed with water, and then dried in air. PAS, PAMS, PHS, PHMS and partially hydrolyzed samples of PAS and PAMS were vacuum dried for about 1 week. The molecular weight (M_n) and the molecular weight distribution (M_w/M_n) were obtained with a Toyosoda gel permeation chromatograph, Model HLC-801. The chromatograph was calibrated by plotting the molecular weight of monodisperse polystyrene (Pressure Chemical Co.) against the elution volume. Values of M_n and M_w/M_n

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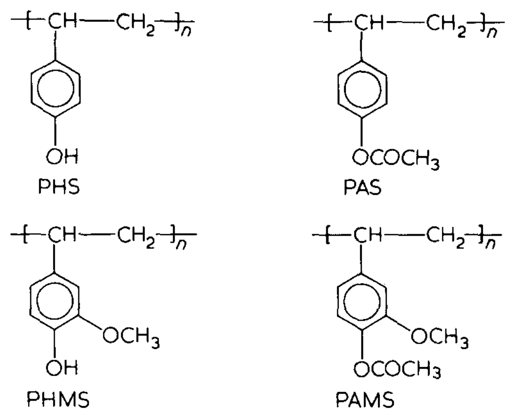

Figure 1 Chemical structures of PHS, PAS, PHMS and PAMS

were 1.0×10^5 and 3.1 for PAS and 2.2×10^5 and 3.2 for PAMS, respectively.

Infrared spectroscopy (i.r.)

A Perkin-Elmer Model 180 grating spectrophotometer was used for i.r. spectrometry. Intensities of absorption bands were calculated by the 'base line method'[7-9], assuming Beer's law. The base-line optical density was calculated from the equation

$$OD = \log_{10}(\mathrm{AB}/\mathrm{CB}) \qquad (1)$$

Where OD is the base-line optical density; CB is the height of the recorded spectrum from zero line to the selected absorption peak; and AB is the distance from zero line to the straight base-line, joining two spectral points located on either side of the absorption peak. AB was measured at the same wave number as CB. AB/CB was calculated after correcting for the emission of the sample. The absorption band for C = O stretching due to the carboxyl group (1750 $\mathrm{cm^{-1}}$) was used as a criterion for degree of hydrolysis. The % relative intensity was calculated from the following equation using the aromatic ring vibration (1500 $\mathrm{cm^{-1}}$) as the standard absorption band,

$$R = \left[1 - \frac{OD_{\mathrm{hy}}(1750)/OD_{\mathrm{hy}}(1500)}{OD_{\mathrm{ac}}(1750)/OD_{\mathrm{ac}}(1500)}\right] \times 100 \qquad (2)$$

where R is the degree of hydrolysis; OD_{hy} is the optical density of partially hydrolyzed PAS or PAMS; OD_{ac} is the optical density of PAS and PAMS.

Differential scanning calorimetry (d.s.c.)

The thermal behaviour of the specimens was observed with a Perkin-Elmer differential scanning calorimeter model DSC-II. The d.s.c. curves were obtained at the scanning rate of 20°C $\mathrm{min^{-1}}$. Samples were sealed in volatile sample aluminium pans. The aluminium pans used in this experiment had been previously exposed to steam in an autoclave at 120°C for 3 h in order to eliminate formation of aluminium hydroxide during measurements. Samples were firstly dried in a vacuum desiccator for about 1 week and then each 3 mg sample was weighed. For measurement on polymer containing sorbed water a small amount of water was added by a microsyringe, then the total weight was measured on a microbalance. If the water content was over the predetermined amount, the sample pan was allowed to stand for a few minutes until the water evaporated. The water content [water content = (weight of water/weight of sample) × 100%] was calculated by measuring the total weight after the sample pan had been sealed. After a d.s.c. measurement, the sample pan was again weighed to confirm that no weight loss had taken place during the scan.

RESULTS AND DISCUSSION

The i.r. spectra of hydrolyzed PAS with various degree of hydrolysis were measured over the range 1400–2000 $\mathrm{cm^{-1}}$. The intensity of the 1750 $\mathrm{cm^{-1}}$ band (C = O stretching) decreased gradually with increasing degree of hydrolysis, then disappeared completely for a 100% hydrolysis. I.r. spectra of PAMS with various degrees of hydrolysis showed similar tendencies, although they are not given.

The degree of hydrolysis was calculated by the 'base-line' method from equation (2). The degree of hydrolysis of PAS and PAMS increased rapidly up to 60% with increasing time of reaction, and then saturated gradually over a period of ~24 h. The rate of the reaction of PAS is more rapid than that of PAMS.

The relationship between the degree of hydrolysis and the glass transition temperature (T_g) is shown in *Figure 2* for PAS and PAMS. The T_g's increase almost linearly with increasing hydrolysis. The T_g's of PHS and PHMS obtained from 100% hydrolyzed PAS and PAMS are 455 K and 415 K, respectively. In our previous paper[5], the variation of the T_g's for styrene derivatives having different kinds of substituent groups has been discussed. With increasing hydrolysis, the acetoxyl group is substituted by the hydroxyl group and accordingly, hydrogen bonds are formed between hydroxyl groups. However, the presence of the methoxyl group attached to the 3-position of the aromatic ring decreases T_g in the case of the partially

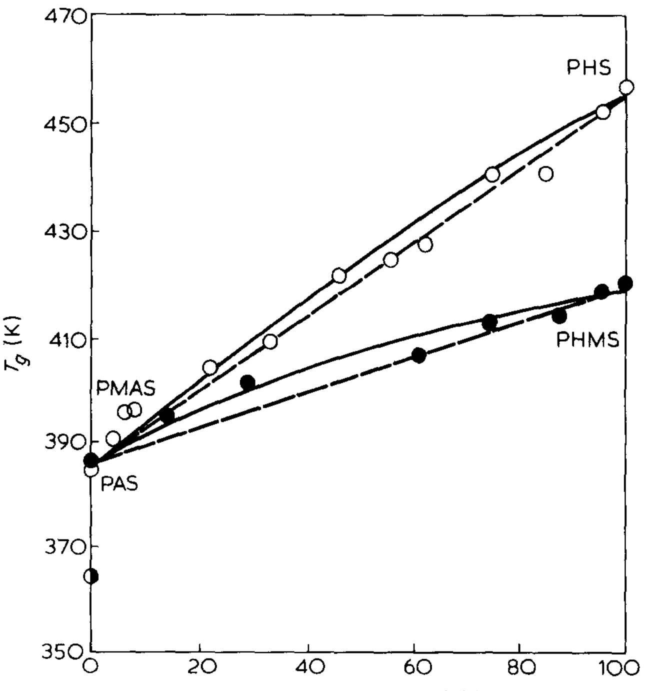

Figure 2 Effect of degree of hydrolysis on the T_g of PAS and PAMS. Dotted line shows calculated values

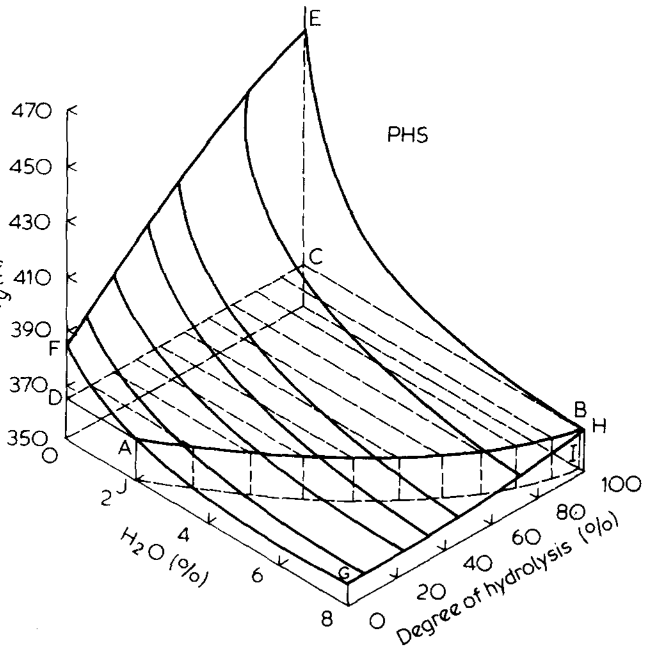

Figure 3 Three dimensional diagram with the T_g on the vertical axis, water content and degree of hydrolysis on the horizontal axes of PAS

hydrolyzed PAMS, as is shown in *Figure 2*. Barb[10] pointed out in his study of the glass transition of monosubstituted vinyl polymers that T_g decreases on introduction of a substituent group at the 3-position. The considerable difference of T_g between PHS and PHMS and the low T_g's of PAS and PAMS compared with values for those of PHS and PHMS, as shown in *Figure 2* will be acceptable if we consider that the presence of a bulky substituent group such as acetoxyl or methoxyl group will disturb the hydrogen bonding[3]. It is also noteworthy that the partially hydrolyzed polymers used in this experiment have both hydroxyl and acetoxyl groups in their substituents.

We attempted to apply the rule of Fox[11] and Wood[12] for T_g of copolymer to partially hydrolyzed PAS and PAMS. The simple equation given by Fox is

$$\frac{1}{T_g}=\frac{W_a}{T_{ga}}+\frac{W_b}{T_{gb}} \qquad (3)$$

where T_g is the glass transition temperature of the copolymer; T_{ga} and T_{gb} are the glass transition temperatures of the homopolymers *a* and *b*; and W_a and W_b are the weight fractions of the constituents. Calculated values are shown as dotted lines in *Figure 2*. It can be seen that the experimental values agree well with the calculated ones. From this result, it is concluded that PAS and PAMS are hydrolyzed randomly; and those have the physical properties of random copolymers.

Above copolymers have different amounts of hydroxyl groups. Accordingly it can be considered that the amounts of hydrogen bonds between molecules change systematically with the degree of hydrolysis of PAS and PAMS; that is, hydrogen bonding increases with the increase of hydroxyl groups obtained by the partial hydrolysis. On the other hand, it is well known that water acts as a breaker of hydrogen bonding. Therefore, as described in the Experimental section, the predetermined amounts of water were added to the samples of partially hydrolyzed PAS and PAMS, which have different amounts of hydroxyl groups, and then the change of T_g of each sample was measured.

Figures 3 and *4* are the three dimensional diagrams for PAS and PAMS with T_g on the vertical axis and the water content and degree of hydrolysis of the polymers on the horizontal axes. In these Figures, the point E shows each T_g of completely hydrolyzed polymers (PHS 455 K in *Figure 3* and PHMS 415 K in *Figure 4*, respectively) and the point F shows each T_g of original acetate polymers (PAS = 385 K, PAMS = 388 K, respectively). The point D shows that T_g of PSt (365 K). The plane ABCD indicates the isothermal plane of the T_g of PSt. The T_g of the pure PHS (100% hydrolyzed PAS) decreases rapidly by addition of water up to 7.8% (line EB), and then it decreases gradually by adding more water. The T_g of PHS in the presence of 7.8% water content is equal to the T_g of dry PSt as shown by the point B. Then because of the plasticizing effect T_g decreases on addition of more water. Moreover, the T_g of PAS hydrolyzed to different degree decreases in a manner similar to that of PHS, but the decrement of T_g is less than in PHS due to addition of the same amount of water if the PAS is partly hydrolyzed. As can be recognized from *Figure 3*, this tendency of the decrement of T_g is obviously correlated with the order of hydrolysis of PAS: 100% > 76% > 49% > 22% > 8% > 0%. In the case of partially hydrolyzed PAMS, as shown in *Figure 4*, the amounts of water which decrease the T_g's of the polymers to that of PSt are ~1.2–4.5% being dependent on the degree of hydrolysis.

In *Figures 3* and *4*, the plane EFGH is separated by the plane ABIJ. The separated plane ABEF has a steep gradient, while the plane ABHG has a dull one. The areas ABEF in both Figures show the decrease of T_g's of partially hydrolyzed PAS and PAMS with the breakage of hydrogen bonds caused by the addition of water. It is also considered that the areas ABHG show the decrease of T_g by plasticizing effect of added water. The above relation can be understood if it is kept in mind that the adsorbed water has only a plasticizing effect in PSt which, owing to lack of hydroxyl group, cannot form any hydrogen bonding. The excess water molecules in partially hydrolyzed PAS and PAMS remain as the bulk water if water content is more than certain amounts which are different by the degree of hydrolysis. This excess water has the plasticizing effect to the polymers.

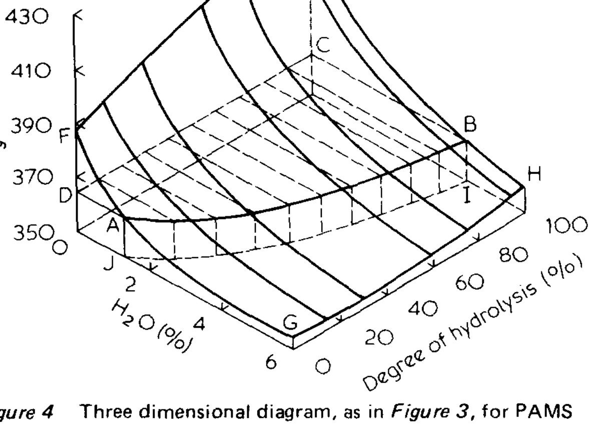

Figure 4 Three dimensional diagram, as in *Figure 3*, for PAMS

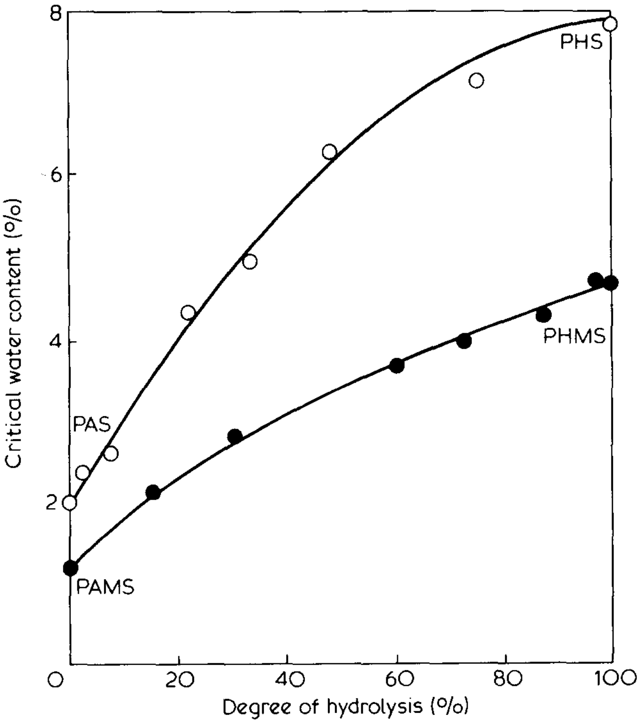

Figure 5 Relation between critical water content and degree of hydrolysis

It can be ascertained, therefore, that water acts initially as a hydrogen bond breaker; that is, hydrogen bonds of OH-groups in PHS and PHMS are broken by a small amount of water and the T_g's of PHS and PHMS decrease rapidly in the region of water content less than 7.8 and 4.5%, respectively. The T_g's of the PHS and PHMS containing above amount of water are similar to the T_g of PSt which has no hydrogen bonding since the hydrogen bonds of the polymers are completely broken by water in this range of water content. Therefore the plane ABIJ which separates the plane EFGH to the two parts is a very important boundary. This plane ABIJ can be considered as defining the 'critical water content'. The critical water content of PAS is ~2.0% and that of PAMS is ~1.2%.

This critical water content is plotted against the degree of hydrolysis in *Figure 5*. As mentioned above, those values were obtained by calculating the necessary water content in order to decrease the T_g's of PAS and PAMS to that of PSt. Here, when it is considered that those three polymers have the similar molecular weight; i.e. PAS is 1.0×10^5, PAMS $= 2.2 \times 10^5$ and PSt $= 2.6 \times 10^5$, it is inferred that the difference of T_g's of dry PAS and PAMS with that of PSt should come from some other reasons except molecular weight. If we consider the chemical structure of PAS and PAMS, it is found that PAS has the acetoxyl group at the 4-position of the aromatic ring and PAMS has the acetoxyl group at the 4-position and the methoxyl group at the 3-position of the aromatic ring. According to Barb[10], if the polystyrene has a substituent group such as methoxyl group, methyl group and ethyl group, the T_g of the polystyrene derivatives decreases ordinarily. However, despite the similar molecular weight, PAS and PAMS have higher T_g's than that of PSt. Moreover, by addition of small amounts of water, the T_g values becomes similar to that of PSt. The above results show that PAS and PAMS should have very weak hydrogen bonds because of the $C=O$ group of acetoxyl group[14]. *Figure 5* also shows that PAS needs more addition of water to obtain the T_g similar to PSt than PAMS because of the presence of methoxyl group at the 3-position of aromatic ring.

From the above results, we conclude that the OH-groups of the substituents in hydrolyzed PAS and PAMS have an important role in hydrogen bonding. The difference between the T_g's of PAS and PAMS may be due to the methoxyl group introduced into the 3-position of the aromatic ring. Water adsorbed on the hydrolyzed PAS and PAMS acts as a hydrogen-bond breaker in the region less than the 'critical water content' and acts as a plasticizer above this region.

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