

# Notes to the Editor

## Differential thermal analysis of styrene derivatives related to lignin

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### INTRODUCTION

Lignin is widely spread in nature and exists abundantly next to cellulose in higher plants<sup>1</sup>. In an earlier paper<sup>2</sup>, we paid attention to the biodegradation of styrene derivatives having pendant quaiacyl groups. These polymers are degraded by microorganisms in the soil.

It is generally accepted that lignin molecules consist of several basic units such as *p*-hydroxyphenyl, guaiacyl and/or syringyl groups which are considered to link with each other in statistically different ways<sup>1</sup>. It is also known that the glass transition temperature of lignin is significantly higher than those of the usual synthetic thermoplastic polymers<sup>3,4</sup>. However, it is difficult to attribute any known cause to the high transition temperature since the high order structure of lignin is very complicated.

In this study, poly(*p*-hydroxystyrene), poly(3-methoxy-4-hydroxystyrene) and the acetates of these polymers were prepared as model polymers whose structure is related to that of lignin; thermal properties of the polymers were investigated, especially from the viewpoint of how hydroxyl and methoxyl groups affect the glass transition temperature. An evaluation of the effect of molecular weight on glass transition temperature of the polymers in comparison with standard polystyrene was also undertaken. At the same time a comparison of the glass transition of the polymers with that of lignin was also made.

### EXPERIMENTAL

#### Sample preparation

*p*-Hydroxystyrene (HS) was prepared

from *p*-hydroxycinnamic acid by a procedure similar to that of Sovish<sup>5</sup>. *p*-Hydroxycinnamic acid (10 g) was added to quinoline (10 ml) containing copper powder (0.2 g), and hydroquinone (0.3 g). The mixture was then heated at 200°C under a nitrogen atmosphere until the evolution of carbon dioxide subsided. The crude reaction mixture was distilled under reduced pressure to separate the monomer from quinoline; the fraction boiling at 90°–100°C (0.5 mmHg) was collected. The crude HS obtained was added to cold 1N hydrochloric acid solution, extracted by ethyl ether (free from peroxide), dried with anhydrous sodium sulphate and purified by distillation. Yield, 4.6 g, 59%.

3-Methoxy-4-hydroxystyrene (MHS) was prepared from ferulic acid by a procedure reported previously<sup>2</sup>.

*p*-Acetoxystyrene (AS) was prepared from HS (5 g) by acetylation with the mixture of pyridine (30 ml) and acetyl anhydride (20 ml). A white oil was obtained. Yield, 4.8 g, 75%.

3-Methoxy-4-acetoxystyrene (MAS) was prepared from MHS by a similar procedure.

PolyAS and polyMAS were obtained by bulk polymerization using 1% of 2,2'-azobisisobutyronitrile (AIBN) as an initiator. To obtain samples having different molecular weights, polymerization temperatures and times were changed from 60° to 100°C and from 0.5 to 8 h according to the predetermined conditions<sup>6</sup>. PolyHS was obtained by the hydrolysis of polyAS. PolyMHS was prepared from polyMAS. Standard polystyrene samples (PST) were commercially obtained from Pressure Chemical Co. Molecular weights ( $M_n$ ) of samples were  $2.00 \times$

$10^3$ ,  $1.03 \times 10^4$ ,  $1.98 \times 10^4$ ,  $9.72 \times 10^4$ ,  $1.60 \times 10^5$ ,  $8.6 \times 10^5$  and  $1.8 \times 10^6$ ; molecular weight distribution ( $M_w/M_n$ ) were from 1.01 to 1.06.

Thio- (TL) and dioxane lignins (DL) were prepared by the procedure reported in the previous papers<sup>7,8</sup>.

### Measurements

A gel permeation chromatograph (Toyo Soda Model HLC-801) was used for determination of molecular weight and molecular weight distribution.

A Perkin-Elmer Model DSC-II differential scanning calorimeter was used for thermal analysis. Glass transition temperatures,  $T_g$ , were determined from a d.s.c. curve as described previously<sup>9</sup>. In order to eliminate traces of water and to get the same thermal history, each sample was heated at 420K for 3 min and then allowed to cool to room temperature. Heating rates were varied from 40 to 2.5 K/min and  $T_g$  values obtained by extrapolating  $T_g$  vs. heating rate curves to zero heating rate.

A Rigaku Denki thermogravimeter was used for thermogravimetry measurements.

### RESULTS AND DISCUSSION

Molecular weight and molecular weight distributions of the samples, calculated from the gel permeation chromatograms are given in Table I. Molecular weights of PHS and related polymers varied

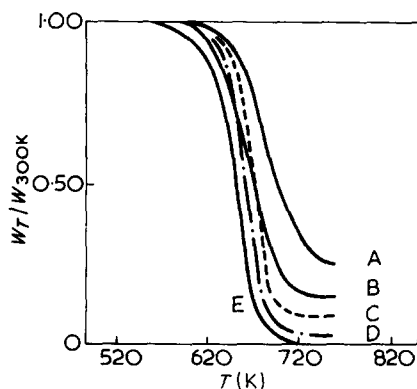


Figure 1 Thermogravimetric curves of PST (E), PHS (A), PAS (C), PMHS (B) and PMAS (D).  $W_T$ , weight at the temperature  $T$ ;  $W_{300K}$ , weight at 300K

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Table 1 Symbols of samples, molecular weight, molecular weight distribution and glass transition temperature at various heating rates measured by d.s.c.

Symbol	$M_n$	$M_w/M_n$	$T_g$ (K) at heating rate (K/min)					$T_g^*$
			40	20	10	5	2.5	
PHS (◇)	$3.7 \times 10^5$	2.6	462	456	449	443	441	440
	$1.0 \times 10^5$	4.3	417	413	410	408	407	406
	$3.6 \times 10^4$	3.5	419	416	413	411	409	408
	$6.6 \times 10^3$	3.4	385	383	382	382	381	380
PAS (△)	$3.7 \times 10^5$	2.6	400	395	394	393	391	390
	$1.0 \times 10^5$	4.3	385	387	387	385	384	383
	$3.6 \times 10^4$	3.5	379	376	375	374	374	374
	$6.6 \times 10^3$	3.4	375	372	371	370	370	370
PMHS (○)	$2.2 \times 10^5$	3.2	416	413	410	409	408	407
	$1.5 \times 10^5$	2.2	398	392	393	390	388	387
	$1.3 \times 10^5$	2.5	391	388	386	384	383	382
	$1.0 \times 10^4$	4.2	362	359	357	357	357	356
PMAS (▽)	$2.2 \times 10^5$	3.2	391	388	387	386	385	384
	$1.5 \times 10^5$	2.2	386	384	383	383	382	381
	$1.3 \times 10^5$	2.5	375	372	371	370	369	368
	$3.3 \times 10^4$	3.3	381	379	378	378	379	378
TL† (□)	$7.5 \times 10^3$			397				
	$6.0 \times 10^3$	1.5		391				
	$4.4 \times 10^3$	1.5		388				
	$4.0 \times 10^3$	1.4		386				

\*  $T_g$  obtained by extrapolating to zero heating rate from  $T_g$  vs. heating rate curve;  
 † Thiolignin (ref 6)

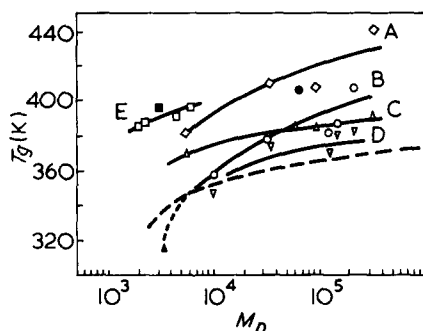


Figure 2 Effects of molecular weight on  $T_g$  of PHS (A), PAS (C), PMHS (B), PMAS (D), and TL (E). (---),  $T_g$  of monodisperse PST; ■,  $T_g$  from d.s.c. of dioxane lignin (DL) (ref 4); ●,  $\alpha_T$ , maximum temperature of damping from torsion braidal analysis (t.b.a.) of PHS (ref 8); ▲,  $\alpha_T$  of PMHS (ref 8)

over a broad range. Commercial polystyrenes were also used as the standard for comparison, although these are not given in the Table. Data for lignins listed in Table 1 are a representative sample from a previous report<sup>7</sup>. As shown in the Table,  $M_n$  values of lignins are small and the molecular weight distribution is rather narrow.

The thermal stability of the samples was determined by thermogravimetric methods. Samples used were stable up to about 570–600K as shown in thermogravimetric curves in Figure 1. The temperatures for the commencement of degradation of the styrene derivatives

were almost the same as those of polystyrene. Activation energies of degradation obtained from assumed first order plots are 40, 70, 55 and 53 kcal/mol for PHS, PAS, PMHS and PMAS respectively. These values accord well with 61 kcal/mol for polystyrene. D.S.C. studies in this experiment were carried out in the temperature region in which each sample was stable during repeated thermal analysis.

Glass transition temperatures of the polymers measured at various heating rates and values extrapolated to zero heating rate are also listed in Table 1. Data for lignins cited in a previous report<sup>7</sup> are also included.

Figure 2 shows the relationship between  $T_g$  and molecular weight for styrene derivatives and lignins. The broken line in the Figure shows  $T_g$  values of monodisperse polystyrenes.  $T_g$  of polystyrene depends markedly on the molecular weight in the low molecular weight region, and then gradually approaches the characteristic value when the molecular weight exceeds  $1 \times 10^4$ . In the case of the lignin,  $T_g$  increases almost linearly with increasing molecular weight within the range measured in this experiment.  $T_g$  for lignin obtained from a different preparative method (DL) showed a similar value<sup>4</sup>.  $T_g$  values for lignins are higher than those for monodisperse polystyrene and other styrene derivatives in the low molecular

weight region. The maximum temperature of damping ( $\alpha_T$ ) measured by torsion braidal analysis (t.b.a.)<sup>10</sup>, which is considered to be an index of  $T_g$ , is also drawn in Figure 2. The values of transition temperature coincide well with those from d.s.c.

The influence of molecular weight on molecular motion of the polymers is clearly recognized; at the same time, the effect of substituent groups is also noteworthy. As seen from Figure 2,  $T_g$  values for PHS and PMHS are 10–50K higher than those of polystyrene and the acetylated samples. This fact seems to show that the introduction of a hydroxyl group at the 4-position of the aromatic ring forms hydrogen bonds and restricts the molecular motion of main chain. On the other hand, if the methoxyl group is introduced in the 3-position of the aromatic ring, adjacent to hydroxyl or acetoxy group at the 4-position,  $T_g$  decreases due to the steric hindrance.

As seen from the above results, it is reasonable to consider that the intermolecular hydrogen bonding due to the hydroxyl group increases the  $T_g$  of PHS, PMHS and lignin. Another factor in the high  $T_g$  of lignin must be attributed to the difference of chemical structure between lignin and styrene derivatives, i.e. lignin has the aromatic ring in the main chains which are assumed to make loose crosslinkage with each other, while the styrene derivative has the aromatic ring pendant from the backbone chain.

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