which average at 0.35[16]. Use of equation (8) yields,

$$4\alpha = T_c^{-1} = 20 \times 10^{-4}\ \mathrm{K}^{-1}.$$

This also is in reasonable agreement with the anticipated value[12] of

$$4\alpha = 25 \times 10^{-4}\ \mathrm{K}^{-1}.$$

A full account of this work, including a reformulation of the theory of the double *T*-jump experiment taking into account the variation of ΔH with relaxation time, will be presented elsewhere.

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Temperature dependence of X-ray diffractograms of amorphous lignins and polystyrenes

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Temperature dependencies of X-ray diffractograms of lignins and polystyrene derivatives were investigated. Bulky side groups, such as methoxyl functionalities were found to expand intermolecular distance, while hydroxyl groups reduce its mean value. Intermolecular distance expands discontinuously at the temperature corresponding to the glass transition temperature.

Keywords Diffraction; measurement; X-ray diffractogram; lignins; polystyrene derivatives; hydroxyl group; temperature; glass transition

The amorphous nature of lignins has been studied by various techniques: broad-line nuclear magnetic resonance[1], differential scanning calorimetry (d.s.c.)[1,2] and viscoelasticity[3].

X-ray diffractometry is a direct method of investigating polymer structure, but its usefulness is restricted to studying amorphous polymers such as lignins. However, the inter- or intramolecular regularity of randomly-packed molecular chains can be interpreted from X-ray analysis of amorphous polymers[4,5].

EXPERIMENTAL

Lignins, polystyrene and polystyrene derivatives used in this experiment are listed in *Table 1*. A sample of polystyrene (PST) with molecular weight distribution (M_w/M_n) of 1.01 were procured from the Pressure Chemical Co. Another sample of polystyrene with M_w/M_n of 3.0 was obtained from the Asahi Dow Chemical Co. Polystyrene derivatives, poly(4-hydroxystyrene) (PHS), poly(4-hydroxy-3-methoxystyrene) (PHMS) and their acetates (PAS, PAMS) and poly(4-methoxystyrene) (PMS) were synthesized as reported previously[6,7]. Isolated lignin, dioxane lignin (DL), methylated DL (MDL) and milled wood lignin (MWL) were prepared according to the procedure reported previously[8].

Table 1 Estimated temperature at which the intermolecular distance expands discontinuously (*T*) and glass transition temperature (T_g)[7]

Sample	M_n	M_w/M_n	*T* (°C)	T_g (°C)
PST	1.0×10^5	1.01	80	83
PST	1.0×10^5	3.0	90	93
PHS	6.6×10^4	2.9	110	100
PHMS	3.2×10^3	2.8	–	75
PMS	2.3×10^3	2.9	70	60
MWL	*	*	130	135
DL	*	*	130	127
MDL	*	*	120	118

* Not estimated, not found

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A Rigaku-Denki 20001 X-ray diffraction analyser equipped with a heating cell was used. A PID controller maintained the temperature of the heating cell to within ±0.1°C. Samples were enclosed in a lead holder with a mica window to maintain sample thickness at temperatures above the glass transition temperature.

A Du Pont type 310 curve analyser was used to resolve the X-ray diffractogram. Gaussian distribution was assumed.

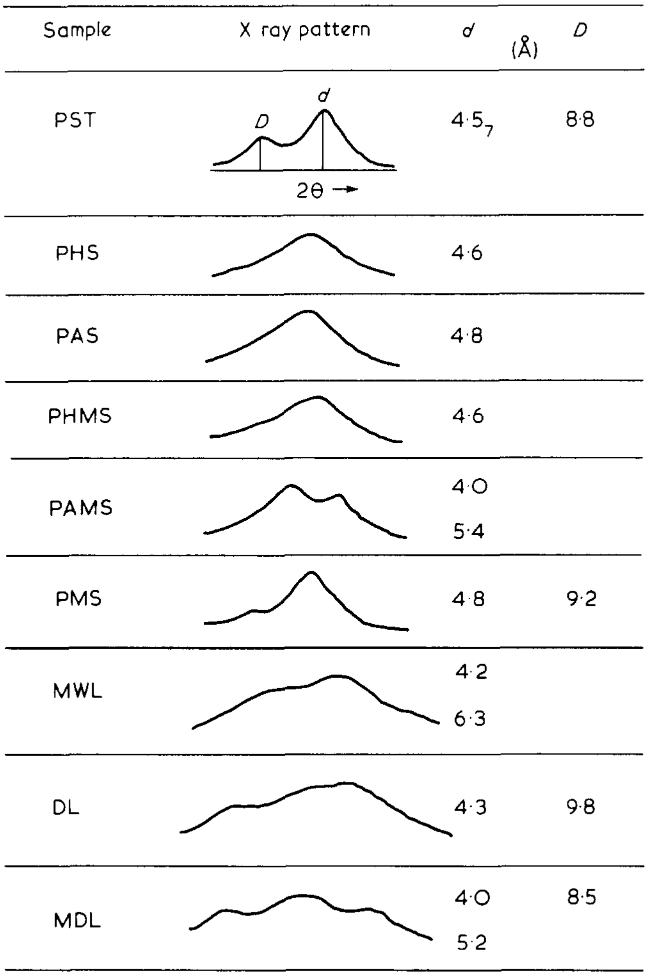
A Toyo Soda gel permeation chromatograph HLC-801A was used for the determination of molecular weight and molecular weight distributions. Tetrahydrofuran was the solvent. Flow rate was 1 ml/min and sample concentration, 0.2 mg ml^{-1}. Narrow molecular weight polystyrene having different molecular weights (Pressure Chemical Co.) were used as standards.

RESULTS

Figure 1 shows X-ray diffractograms of samples at 20°C. Characteristic diffuse haloes were observed for all samples. Two peaks, at 4.6 and 8.8 Å, were observed for PST. However, only one peak was observed at 4.6–4.8 Å for PHS, PAS, PHMS.

For PMS, two peaks were observed. The inner halo was smaller than that for polystyrene.

MWL, DL and MDL showed broad X-ray diffractograms having several peaks. The outer halo of DL observed at 4.3 Å was separated into two peaks at 4.0 and 5.2 Å when the hydroxyl groups (DL) were substituted with methoxyl groups (MDL). Accordingly we inferred that the methoxyl groups expand the intermolecular distance in lignin.



Sample	X ray pattern	d (Å)	D
PST		4.5_7	8.8
PHS		4.6	
PAS		4.8	
PHMS		4.6	
PAMS		4.0 5.4	
PMS		4.8	9.2
MWL		4.2 6.3	
DL		4.3	9.8
MDL		4.0 5.2	8.5

Figure 1 X-ray patterns of polystyrene, polystyrene derivatives and lignins

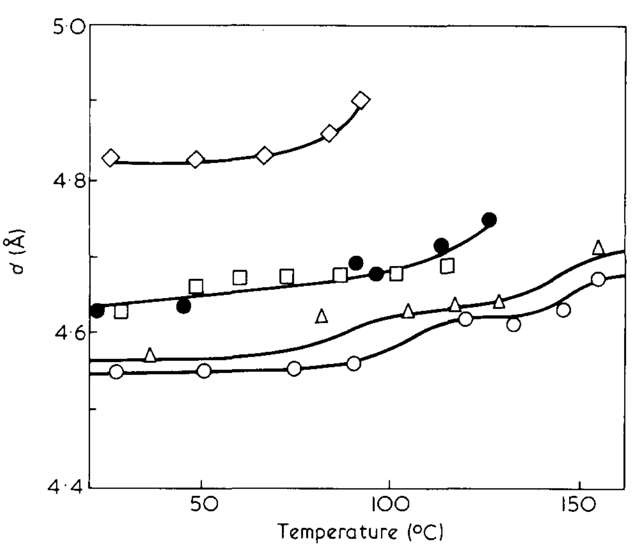


Figure 2 Temperature dependence of the intermolecular distance of polystyrenes and polystyrene derivatives: △, PST ($M_n = 1.0 \times 10^5$, $M_w/M_n = 3$); ○, PST ($M_n = 1.0 \times 10^5$, $M_w/M_n = 1.01$); ●, PHS; □, PHMS; ◇, PMS

The inner halo for polystyrene is related to the intermolecular distance[5,6,9]. This is supported by the fact that the diffuse halo is concentrated on the equatorial line when the polystyrene monofilament is stretched. The outer halo is attributed to the intra- and intermolecular distances, reflecting the regularity of the benzene ring. It is reasonable to assume that the broad distribution of 2θ values shown in *Figure 1* corresponds to the statistical distribution of inter- and intramolecular distances, indicating the amorphous nature of the samples. We calculated mean values of intra- and intermolecular distance from those 2θ angles where the strongest intensity was observed for each halo. The calculated values of Bragg spacing are listed in *Figure 1*.

Figure 2 shows the temperature dependence of the intermolecular distance, calculated from the 2θ angle of outer halo for the two kinds of polystyrene and the three polystyrene derivatives. It was found that a characteristic temperature, corresponding to the glass transition temperature (T_g), was observed when the intermolecular distances increased discontinuously. The intermolecular distances of PHS, PHMS and PMS were larger than those of the unsubstituted polystyrenes over the whole range of temperature. This indicates that the bulky side chain, especially the methoxyl group introduced into the 4-position of benzene nucleus, expands the intermolecular distance.

Figure 3 shows the temperature dependence of the intermolecular distance for DL and MDL. The distance shown for MDL in the Figure represents the mean value of two broad peaks at about 4.0 and 5.2 Å. It was found that the temperature at which intermolecular distance increases is lower for MDL than DL. The temperature values correspond to the respective T_gs. As shown in *Table 1*, the transition temperature values (T) measured by X-ray diffractometry are similar to the T_gs obtained by

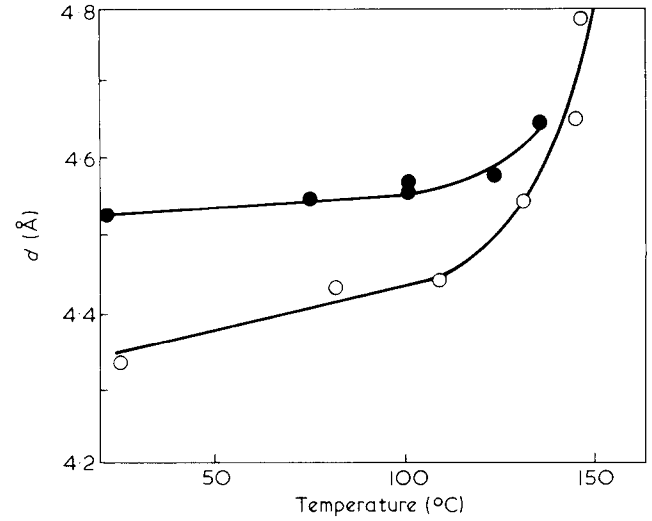


Figure 3 Temperature dependence of the intermolecular distance calculated from main peak of halo pattern of lignins. ○, DL; ●, MDL

differential scanning calorimetry[7].

CONCLUSIONS

Thus bulky side groups, such as methoxyl functionalities, expand intermolecular distances. Hydroxyl groups reduce the mean intermolecular distance, as estimated from the increase in halfwidth of each Gaussian distribution for each reflection observed in X-ray patterns of PHS and PHMS. The broad and plateau-like haloes of the lignins seem to be attributable to molecular irregularity and randomness in the first-order structure and inter- and/or intramolecular hydrogen bonding. X-ray patterns of samples obtained at a series of temperatures between 20° to 200°C showed that the intermolecular distance expanded discontinuously at a temperature corresponding to the glass transition temperatures of the lignins and their related polymers.

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