The Absolute Molecular Weight Distribution of Hydroxypropylated Lignins

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ABSTRACT: The molecular weight distribution of hydroxypropylated lignins was determined by using GPC/LALLS and GPC/DV. VPO was used to provide a reference number average molecular weight to compare with the values obtained by GPC. GPC/LALLS results were complicated by absorbance, fluorescence, and the need for a polarization correction. GPC/DV proved to be a reliable and convenient means of obtaining an absolute molecular weight distribution for the lignin derivatives. The results showed that a time-dependent association was occurring.

Introduction

Lignin is a bipolymer that ranks second in natural abundance only to cellulose. Due to its profusion, variety, and properties, the potential for technological applications is tremendous.[1,2] Before these latent possibilities may be realized however, it is necessary to understand the structure/property relationships for this type of material. At the heart of this requirement is the need to determine absolute molecular weights and molecular weight distributions for lignins.

A literature review will reveal that the usual methods for molecular weight determination include the use of vapor-phase osmometry[3-6] or ultracentrifugation.[7-11] These techniques involve the tedious fractionation of this highly polydisperse polymer in order to obtain its molecular weight distribution. In addition, proper calibration of the VPO is critical for accurate data acquisition and the application of ultracentrifugation to lignins is fraught with difficulties.[7,10] With the relatively recent advent of gel permeation chromatography (GPC), most investigators have turned to this instrument for lignin characterization due to its ease of use and short analysis time.[3,4,6-8,12-28] However, the GPC molecular weights and hence molecular weight distributions typically obtained thus far have only been relative quantities since the calibration method commonly used was based on the molecular weights of polystyrene standards, which are structurally and topologically very different from lignins. In an attempt to obtain absolute numbers while bypassing the use of calibration standards with substantially different chemical structures, Kolpak et al. have resorted to a dual detection system for GPC that utilized both a differential refractive index (DRI) detector and a low-angle laser light scattering (LALLS) detector.[3] However, the use of GPC/LALLS to study lignins has complex problems associated with it that make its application to lignin analysis difficult.

About 20 years ago, Benoit et al. demonstrated that GPC separates molecules according to their hydrodynamic volume, which may be calculated by taking the product of intrinsic viscosity and molecular weight.[29] In order to obtain absolute molecular weights, it is thus necessary to calibrate the instrument based on molecular size and not molecular weight as is the usual practice. To take advantage of Benoit's universal calibration curve, one must be able to measure the intrinsic viscosity of the standards and the samples as they elute from the chromatograph. In this connection, a number of online viscosity detectors have been developed recently.[30-41] Their use is still limited however since most of these detectors were one-of-a-kind models. In fact, only one is commercial.[40,41] Aside from the fact that viscosity detectors are not readily available, there is another reason for their lack of use in lignin research. There appears to be a reluctance to apply the universal calibration concept to lignins because of the prevalent belief that lignins have a three-dimensional network structure which invalidates the procedure. However, no research has appeared to provide support for this viewpoint.

It is the objective of this investigation to show the feasibility of using GPC with a differential viscosity detector (GPC/DV) for the analysis of lignin molecular weights and molecular weight distributions. This was achieved by simultaneous use of the DRI as the concentration sensitive detector, the LALLS, and the DV. VPO was used to provide reference values for the average molecular weights obtained.

In the course of the work, some anomalies due to the acknowledged association of lignin macromolecules were encountered.[4,7,8,12,13,42-44] This added aspect of lignin behavior shall also be explored and emphasized as important. Hydroxypropylated lignins were the actual materials investigated.

Gel Permeation Chromatography (GPC). Gel permeation chromatography appears to be the most popular technique for the determination of lignin molecular weights and molecular weight distributions, no doubt due to its ease of use and convenience.[4-8,12-16,18,21,24-27,45-53] Typical GPC analyses utilize columns based on cross-linked dextran or polystyrene cross-linked with divinylbenzene. There has been rarely usage of silica gel columns. Analyses tend to be carried out with aqueous sodium hydroxide systems or with organic solvents such as dioxane, tetrahydrofuran, or dimethylformamide with LiCl or LiBr. The columns may be calibrated either by using narrow molecular weight distribution polystyrene standards, lignin model compounds, or narrow fractions of lignin samples whose molecular weights were determined by ultracentrifugation. In most cases, polystyrene standards have given reasonable values of molecu-

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lar weights; however, it was found that these standards were not suitable for molecular weight determination of lignin derivatives. For these modified lignins, derivatized lignin model compounds were more appropriate.[46] Caution must be exercised in assigning molecular weights using this type of calibration because this method yields *apparent* and not *absolute* molecular weights.

GPC Multidetection. The detector typically used for GPC analysis is the concentration sensitive detector, usually an ultraviolet or a differential refractive index detector. An early attempt at using multidetection in GPC was made by Kolpak et al.[3] These authors used GPC with both a DRI and a low-angle laser light scattering (LALLS) detector. The lignin solutions were highly colored, and the concentrations used absorbed a significant amount of the incident light. A correction, particularly significant with more concentrated solutions, was applied for static LALLS measurements to obtain second virial coefficients for GPC/LALLS. Also, the lignins were shown to fluoresce, although the fluorescence was claimed to be minimal at 633 nm, the analysis wavelength.[3] A filter was installed to remove this extraneous radiation. Inspite of these precautions however, the number average molecular weight obtained by LALLS was found to be about three times greater than that obtained by VPO. This may be related to a very recent finding that a third factor, related to beam polarization, needs to be considered in the experiment. This approach reportedly reduces the molecular weights obtained by 30–40%.[54,55]

Association of Lignins. There is quite a bit of evidence that lignins associate in solution. Most of the work done in this area involved kraft lignins and organosolv lignins. The first evidence for association of lignins appeared in the work by Benko in 1964.[42] Additional proof of lignin association surfaced in VPO experiments by Brown, who found that the apparent molecular weight values obtained were dependent on the solvent power of the solvent used to make the solutions.[4] The molecular weight decrease in the respective solvents was accompanied by an increase in the second virial coefficients. Hydrogen-bonded complexes of lignin with the highly polar solvents were postulated.

The association of the lignin molecules has been revealed by multimodal peaks in GPC chromatograms. Also the reduced viscosity plots for these kraft lignins exhibited rather pronounced curvature even for samples that were supposed to be dissociated as well. Time-dependent changes in intrinsic viscosities as a function of solvent and temperature were observed. It was suggested that long-range van der Waals forces played an important role in lignin association.[12]

McCarthy et al. discovered that addition of LiCl or LiBr to the GPC eluant effected a change from the bimodal chromatographic peak which resulted from molecular association to a single broad peak. It was proposed that the salt shielded dipoles in the individual molecules, thus preventing association. Further studies showed that when the fractions from the bimodal molecular weight distribution of lignins were collected and rechromatographed, the materials from the higher and lower end of the distribution were chemically different though not vastly different in molecular weights.[7]

The effect of solvent type was emphasized in further work by McCarthy et al.[8] They demonstrated that apparent molecular weight distributions obtained by using organic solvents were multimodal, extending to very high molecular weights and molecular weights of the associated complexes could be up to 3 orders of magnitude higher than those for the individual components. On the other hand, those obtained by alkaline aqueous eluants tended to be a broad envelope of components with some detailed information in the lower molecular weight region. Again, a time effect was evident as molecular weight increased after some storage time. It was suggested that association occurred in two steps where initially a rapid equilibrium between the associated complexes and the dissociated components exists. The interaction between these two materials was proposed to be highly specific in the sense that high molecular weight species prefer to interact with the low molecular weight materials. The second step was a slow change that may be conformational in nature. In this step, the dissociated species were postulated to convert to a form which made reassociation inaccessible. McCarthy et al. proved hydrogen bonding was not involved by showing that exhaustive methylation and acetylation of the lignins did not significantly affect the amount of high molecular weight species present. On the basis of the available data, the proposed cause for association was the existence of some intermolecular orbital interaction of the HOMO–LUMO type.[8,13,43,44]

Utilization of THF by some researchers recently revealed that bimodality of the chromatograms due to the solvent was not evident. However, there was evidence for an increase in apparent molecular weights over time.[3,20,28,46]

Experimental Section

Materials. Hydroxypropyl (HPL) derivatives of four lignins were studied. The first sample was the HPL derivative of an organosolv red oak lignin. This was obtained by reacting a red oak organosolv lignin with propylene oxide according to a procedure described by Wu and Glasser.[56] The organosolv pulping experiment was performed at an industrial pilot plant using aqueous methanol and 1% sulfuric acid as pulping medium. The reaction product with propylene oxide was isolated from homopolymer by liquid/liquid extraction with hexane from acetonitrile solution, and it was precipitated in water.

The second sample was designated as RO:PO. This was a different batch of the red oak HPL above, produced in larger quantity to allow preparative fractionation.

The third sample was aspen organosolv lignin HPL, made from a lignin supplied by the Biological Energy Corp. of Valley Forge, PA. This lignin was isolated from aspen by pulping with aqueous ethanol and a trace of sulfuric acid followed by hydroxypropylation.[56]

The last sample was a hydroxypropyl derivative of a Westvaco hardwood kraft lignin. A kraft lignin supplied by Westvaco, Charleston, SC, was isolated from a commercial kraft cook of mixed hardwood species by acidification of the spent pulping liquor and then hydroxypropylated.[56]

Vapor-Phase Osmometry. Vapor-phase osmometry was conducted on a Wescan Model 233 at 30 °C on the first day and the third day of sample solution preparation. The lignin solutions were made up with HPLC grade tetrahydrofuran (THF). On the first day of sample preparation, injections were completed within half an hour of solution. Number-average molecular weights were obtained by multistandard calibration.[57]

Specific Refractive Index Increment (dn/dc) Measurements. The solutions made from the four HPL's varied from a pale golden yellow to almost brown in color depending on the concentration. This was important in the selection of the concentration range to utilize in the dn/dc determination. Typically, it is desirable to pick a minimum concentration for which the deflection on the meter of the Chromatix KMX-16 laser differential refractomenter is at least 2000. This was not possible for the lignins because at these "ideal" concentrations, the absorbance of the incident beam by the solutions was significant enough so that the transmitted power reaching the detector was inadequate. The solution to this problem involved a two-step process. First, the refractometer was calibrated so that the maximum concentration of the salt solution used for the standard calibration procedure caused the refractometer meter

Table I
UV-Vis Absorbance of THF Solutions at 633 nm

lignin	concn, g/L	absorbance	ϵ, mL/(g·cm)
red oak	0.997	0.019	44.375
	2.541	0.087	
	5.052	0.203	
	7.582	0.324	
	9.912	0.408	
RO:PO	0.966	0.032	32.202
	1.509	0.044	
	2.053	0.064	
aspen	0.954	0.051	55.935
	1.455	0.080	
	2.061	0.113	
Westvaco	1.100	0.045	33.011
	1.520	0.059	
	2.009	0.075	

to deflect to 2000. Secondly, UV-vis absorbance of the solutions at 633 nm were measured over a range of concentrations in order to determine the conditions at which the solutions had an absorbance of 0.1. These experiments were conducted on a Perkin-Elmer 552 spectrometer at 633 nm with a path length of 1 cm. The results of this experiment are given in Table I. On the basis of these findings, the concentrations used for the experiment were chosen such that they had absorbances which are substantially below 0.05. All measurements were taken at 27 °C. The specific refractive index increments were determined immmediately after the solutions were made and then again on the third day after sample preparation.

Static Low-Angle Laser Light Scattering. The concentrations of the solutions used for the light scattering experiments were chosen based on the UV-vis absorbance experiment conducted for the dn/dc measurement. The requirement that the absorbance of the solutions used for the static light scattering experiment be lower than 0.1 is even more critical here than in the refractive index increment experiment because a large amount of absorbance would result in a significant reduction of the elastic scattering intensity, yielding erroneous results. The solutions were filtered through a 0.2 μm Acrodisc CR filter as they came out of the syringe pump at the rate of 0.15 mL/min and again just before they entered the sample cell. This dual filtering was found necessary for the THF solutions because particulate matter interfered significantly in the scattering measurements, since THF is a low scattering medium, having a Rayleigh scattering factor of 4.4×10^{-6}. The static measurements were carried out on a Chromatix KMX-6 LALLS photometer which was equipped with a 2-mW He-Ne laser operating at 633 nm and an interference filter after the solution to remove any radiation due to fluorescence. The temperature in the sample chamber was 27 °C. The experiments were conducted at a 6-7° forward scattering angle immediately after sample preparation. They were repeated on the third day after sample preparation for different aliquots taken from the same set of solutions. No polarization corrections were applied. Data were analyzed by the standard methods found in the KMX-6 manual.

Gel Permeation Chromatography. Polymer Laboratories narrow distribution polystyrene standards with peak molecular weights of 1250, 2150, 3250, 5000, 9000, 34 500, 68 000, and 170 000 g/mol were dissolved in HPLC grade THF. These were used to construct the universal calibration curve required to determine molecular weights and molecular weight distributions with the differential viscosity detector. These quantities were considered absolute parameters since the calibration curve generated would be the same regardless of the chemical structure of the standards used.

Approximately 2.5 mg/mL solutions of the lignins were prepared in HPLC grade THF. These samples were analyzed on a Waters 150C ALC/GPC equipped with a differential refractive index detector in series with a Chromatix KMX-6 LALLS and having a parallel connected Model 100 differential viscosity detector (Viscotek). Six columns having pore diameters of 500, 10^3, 10^4, 10^5, 10^6, and 100 Å were mounted in series in the chromatograph and maintained at 30 °C. A 200-μL sample was injected, and a flow rate of 1 mL/min was used.

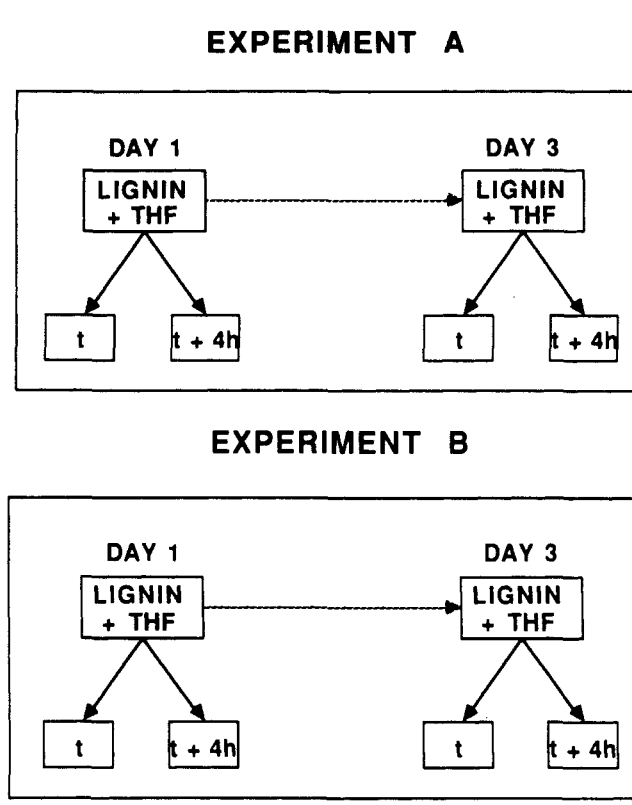

Figure 1. GPC sample management scheme.

Table II
$\bar{M}_n$ from Vapor-Phase Osmometry

sample	day	slope	intercept	correlatn	$\bar{M}_n$, g/mol	% diff
red oak	1	4.697	-0.030	0.9996	1416	17.3
	3	3.962	4.519	0.9978	1684	
RO:PO	1	5.982	0.367	0.9994	1108	19.5
	3	4.929	12.348	0.9986	1348	
aspen	1	4.775	-1.621	0.9982	1393	19.3
	3	3.946	6.492	0.9997	1691	
Westvaco	1	4.441	-1.226	0.9994	1499	21.0
	3	3.614	5.071	0.9963	1850	

The scheme for GPC sample management is given in Figure 1. On the first day, duplicate runs for each sample were made at time "t" within 5 min of sample preparation. This sample was designated as A1(t). Four hours later, a second chromatogram was taken on the same stock of solution and designated as A1(t + 4). The same stock solutions were retested in the same fashion 3 days later with these duplicate runs 4 h apart. The first of these solutions will be designated as A3(t) and the duplicate as A3(t + 4). This entire set of experiments was carried out again on new solutions in order to evaluate reproducibility. The new tests will be referred to as B1(t), B1(t + 4), B3(t), and B3(t + 4) with the annotations having the same meaning as explained above.

Results and Discussion

Vapor-Phase Osmometry. A nontraditional calibration curve was used in the determination of the molecular weights of the lignins by VPO. Details of this multistandard calibration will be published elsewhere.[57]

A summary of the results is given in Table II. In all of these experiments, the data were linear. The intercept of all of the ΔV vs graphs for the first-day experiments were lower than those data on the third day. Except for RO:PO, the ΔV at zero concentration was close to zero, as expected. Another common feature for all experiments was a decrease in slope of these ΔV vs c analyses on the third day compared to the first day tests. This was an indication of an increase in *apparent* molecular weights over time. The apparent number average molec-

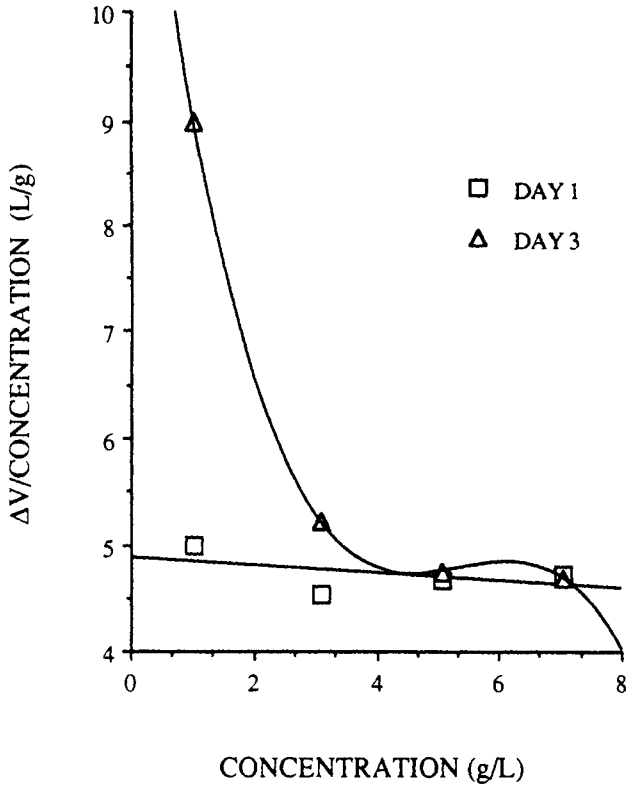

Figure 2. ΔV/concentration versus concentration plot for red oak HPL lignin.

ular weights obtained from the third day investigations were consistently about 20% higher than found on the first day for the same solution. The findings obtained in this experiment are in agreement with observations on the association that lignins are known to undergo.[4,7,8,12,13,42-44]

Further proof of HPL association was revealed from graphs of ΔV/concentration against concentration as shown in Figure 2 for the red oak sample. The slope of such graphs is proportional to the second virial coefficient of the solution, which is an indication of solvent–polymer interaction. In all cases, the data from the first-day experiments were linear when treated as in Figure 2. The slopes of such plots for red oak and for RO:PO were slightly negative while those for aspen and Westvaco hardwood were slightly positive. There was a dramatic difference in second virial coefficients obtained from the third-day experiments. First, the points were better fitted to higher order equations, and second, the slope of the $\Delta V/c$ vs c lines for the more dilute solutions were highly negative. This behavior is typically indicative of association in solution. In this case, the apparent higher molecular weights were due to association which was aided by a diminished interaction between the macromolecule and the solvent.

As previously indicated, the number-average molecular weights, $\bar{M}_n$, obtained by VPO will be used as reference values for the GPC experiment. The $\bar{M}_n$ reproducibility was excellent as long as the time-dependent changes described above were taken into consideration.

Specific Refractive Index Increment (dn/dc). The specific refractive index increments measured on the first day and the third day of sample preparation are shown in Table III. If $\Delta n/c$ were plotted against concentration, a zero slope should result for ideal solutions. For red oak HPL the most notable feature of these graphs is that the $\Delta n/c$ values obtained on the third-day experiments were much higher than those obtained on the first day. With error bars representing the standard deviation in five repetitions for the experiment, there was no overlap of error bars in all the data so the changes noted were real.

Table III
Specific Refractive Index Increments of HPL Lignins

sample	day	dn/dc, mL/g	error	% diff
red oak	1	0.145	0.016	9.2
	3	0.159	0.017	
RO:PO	1	0.139	0.026	37.0
	3	0.202	0.033	
aspen	1	0.152	0.017	80.0
	3	0.358	0.030	
Westvaco	1	0.163	0.023	58.6
	3	0.298	0.026	

The results for RO:PO revealed features similar to red oak HPL. A plot of Δn/concentration versus concentration for the aspen HPL indicated that the results for the first day had a slope of approximately zero. On the third day, however, there was a significant increase in the magnitude of the $\Delta n/c$. The Δn/concentration values for the more dilute solutions were higher than those of the more concentrated solutions. Finally, the results for Westvaco kraft lignin HPL were similar to aspen HPL in that there was no concentration dependence of Δn/concentration on the first day of experiments. However, there was clear curvature in the plot by the third day after the solution preparation, with values of Δn/concentration being much higher on the third day than on the first.

In view of the concentration dependence discovered for most samples, the dn/dc values used were obtained by taking the intercept of the Δn/concentration versus concentration plots. The lack of precision in dn/dc was aggravated by the small quantities weighed out for the dilute solutions required in the experiment. Table III contains a column indicating the percent difference in the values for both days. Except for the red oak solutions, the differences in dn/dc between the first-day and the third-day experiments were significant. This would considerably affect the molecular weights calculated by static LALLS since this quantity is squared in the calculations.

Static Low-Angle Laser Light Scattering (LALLS). The results for static LALLS are shown in Figure 3 for aspen HPL. This static experiment was done in order to get a second virial coefficient for each solution investigated. The second virial coefficient may be calculated as one half of the value of the slope of a plot of $Kc/\bar{R}_\theta$ versus concentration. Typically, one obtains a linear plot. However, none of the HPL solutions exhibited such behavior. All the analyses had some curvature to them both on the first-day and the third-day experiments. Although there was some reproducibility in the shape of the curves for all samples, there was no clear pattern to the deviations from ideality. Thus, it was impossible to measure the absolute weight-average molecular weight from the static LALLS investigations. In any case, the more important parameter here was the second virial coefficient that was necessary for the GPC/LALLS experiment. Since it was obvious that an accurate value may not be obtained due to the complex nature of these solutions, the data from VPO were used instead. This was a reasonable course of action since the same solvent and temperature were used in both the VPO and the GPC experiments. The static LALLS results are cited above to indicate to other workers the problems with solutions that contain materials which can associate and to suggest the following alternative.

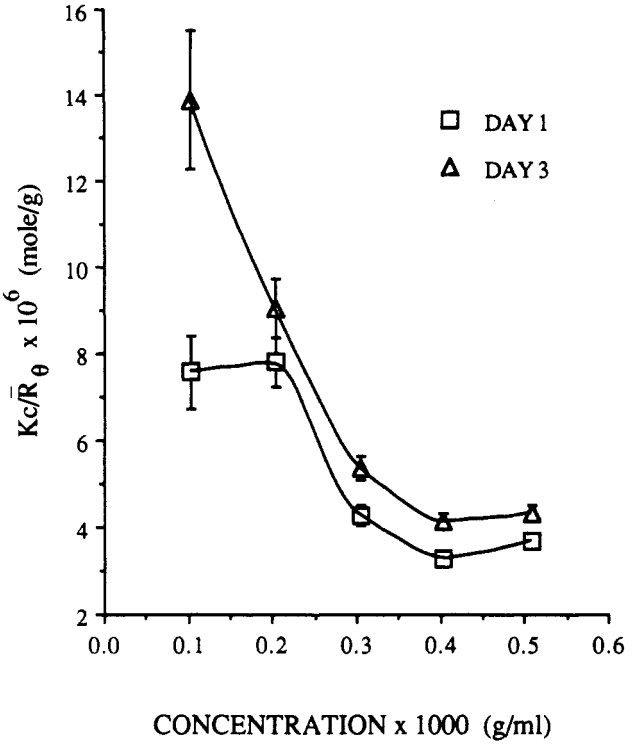

Figure 3. $Kc/\bar{R}_\Theta$ versus concentration plot for aspen HPL lignin.

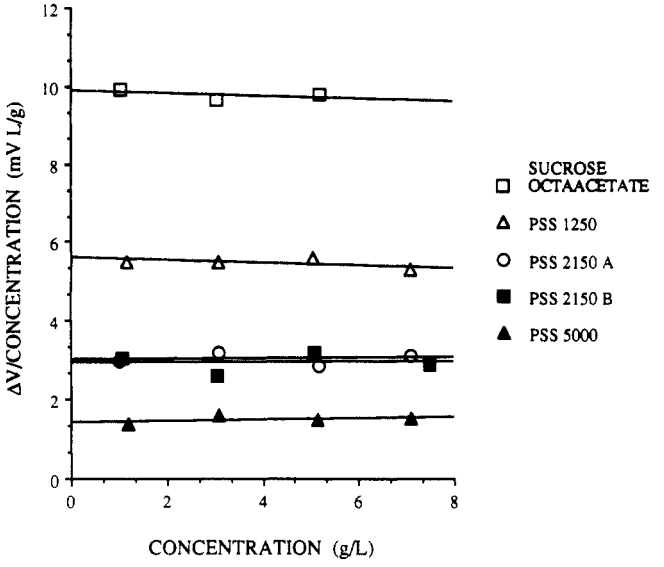

Figure 4. ΔV/concentration versus concentration plot for calibration standards.

The equation appropriate in the VPO calculations is

$$\frac{\Delta V}{c} = K\frac{1}{\bar{M}_n} + A_2 c$$

where ΔV is the voltage change brought about by the temperature rise to compensate for the lower solvent vapor pressure in the solution, c is the concentration, A_2 is the second virial coefficient, $\bar{M}_n$ is the number average molecular weight, and K is an instrument constant. K is the intercept of the plot of $\Delta V/c$ versus c for the calibration standards. There is a clear dependence of K on molecular weight as shown in Figure 4. The K used to calculate the second virial coefficient of the lignins was that obtained for a polystyrene standard with a molecular weight of 1250 g/mole. This choice was based on the VPO results which indicated that the molecular weight

Table IV
A_2 Calculated from VPO Results

sample	$10^3 A_2$, mol cm^3/g^2
red oak	−6.33
RO:PO	−15.35
aspen	−1.12
Westvaco	20.23

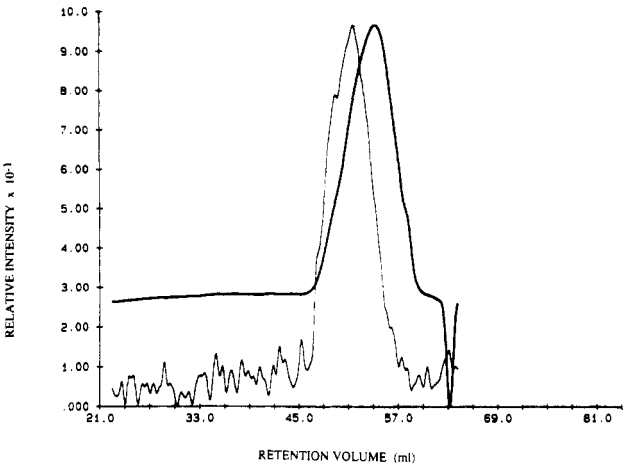

Figure 5. GPC/LALLS dual chromatogram for red oak A1(t).

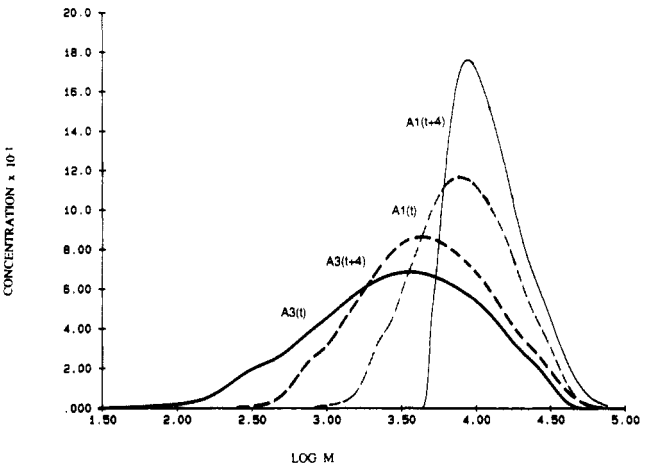

Figure 6. Absolute molecular weight distributions for red oak A.

of this standard was closest to those of the HPL samples. The values of A_2 calculated for the first-day experiments are given in Table IV. These values were used for both the first-day and the third-day experiments in GPC/LALLS, since those are the data points that may be plotted to yield a straight line from which a slope may be calculated. This was deemed to be an acceptable procedure in view of the nature of the $\Delta V/c$ plots for the work on the third day as illustrated in Figure 2.

GPC/LALLS. An example of the data taken by GPC/LALLS for red oak HPL A1(t) is shown in Figure 5. The bold trace is from the differential refractive index (DRI) detector, and the finer trace is from the LALLS signal. The higher noise level in the LALLS signal is due to the low sensitivity of this instrument in the detection of polydisperse low molecular weight polymers.

Figure 6 contains a comparison of the absolute molecular weight distributions obtained for red oak A1(t), A1(t + 4), A3(t) and A3(t + 4). The molecular weight distribution appears to be constantly changing over time. On the first day red oak A1(t + 4) contained a significantly greater amount of high molecular weight material than A1(t), but on the third day, A3(t) had more low molecu-

Table V
Results from GPC/LALLS

sample	set	day	time	$\bar{M}_n$, g/mol	$\bar{M}_w$, g/mol	polydispersity
red oak	A	1	t	6708	11500	1.72
	B	1	t	2710	11170	4.12
	A	1	$t+4$	9441	12320	1.30
	B	1	$t+4$	4371	11690	2.68
	A	3	t	1701	7565	4.45
	B	3	t	4906	10120	2.06
	A	3	$t+4$	3185	8265	2.59
	B	3	$t+4$	2658	6400	2.41
RO:PO	A	1	t	5433	11470	2.11
	B	1	t	9326	14760	1.58
	A	1	$t+4$	5968	12570	2.11
	B	1	$t+4$	5300	11980	2.26
	A	3	t	2459	4470	1.82
	B	3	t	1578	3826	2.42
	A	3	$t+4$	1312	4095	3.12
	B	3	$t+4$	3534	4055	1.15
aspen	A	1	t	4004	24070	6.01
	B	1	t	6470	22540	3.48
	A	1	$t+4$	6560	23310	3.55
	B	1	$t+4$	5311	22140	4.17
	A	3	t	2205	3311	1.50
	B	3	t	2190	3501	1.60
	A	3	$t+4$	1004	3813	3.80
	B	3	$t+4$	822	3426	4.16
Westvaco	A	1	t	3711	17120	4.61
	B	1	t	12430	21810	1.76
	A	1	$t+4$	6322	19460	3.08
	B	1	$t+4$	3714	17320	4.66
	A	3	t	2386	4741	1.99
	B	3	t	858	4872	5.68
	A	3	$t+4$	2139	5350	2.50
	B	3	$t+4$	1608	2518	1.57

lar weight species than A1(t + 4). The distribution shifted toward higher molecular weights once more for A3(t + 4). The absolute molecular weight averages for this sample are shown in Table V. Although the values of molecular weights were not exactly reproducible between sets of experiments, the trends were consistent for the first day of the experiment; the molecular weights increased within 4 h of sample preparation. On the third day, the trend between the two sets of samples were reversed. For set A, the molecular weights increased with time, while they decreased for set B. The dispersity generally decreased within the day. The complex nature of the associations that are occurring within these solutions was again illustrated by the GPC/LALLS results. The fact that the average values of $\bar{M}_n$ obtained are in general larger than those from the VPO experiment is attributed to the lack of a polarization correction in the experiments. However, the general time dependence of the results is correct and the most important point of these GPC/LALLS experiments.

RO:PO. In Figure 7 are shown the molecular weight distribution of RO:PO on the first day and on the third day of sample preparation. It appears that the RO:PO molecular weight increased slightly on the first day and then decreased continuously afterwards as seen in the data for RO:PO A3(t) and A3(t + 4). However, as in the case of red oak, this trend was not reproduced with a second set of experiments. All average molecular weights are displayed in Table V. It is obvious that for experiment set B, the molecular weights were lower on the third day compared to those on the first day. However, in contrast to the first set of solutions, the molecular weights of RO:PO B3(t + 4) were higher than those of RO:PO B3(t). Also in contrast to red oak, the molecular weights of RO:PO were generally lower on the third day than on the first day of solution preparation. These differences

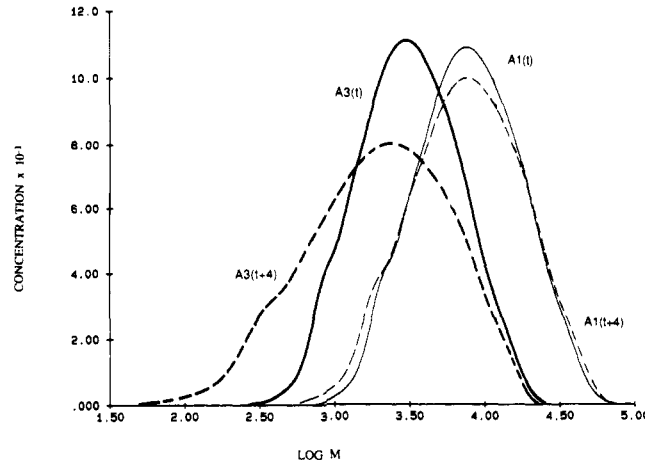

Figure 7. Absolute molecular weight distributions for RO:PO A.

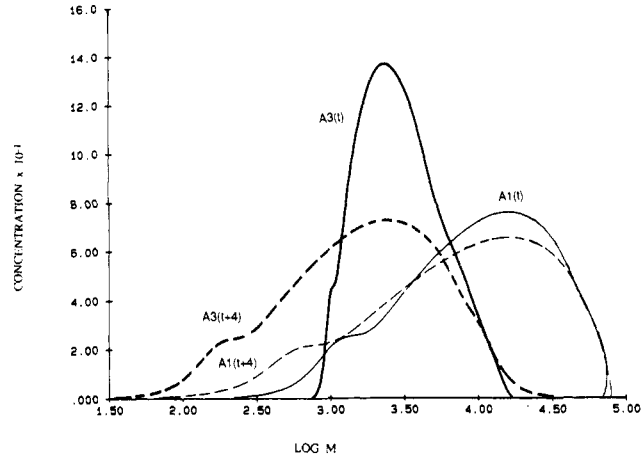

Figure 8. Absolute molecular weight distributions for aspen A.

were unexpected because RO:PO is supposed to be identical to red oak, yet the association pattern seems to be different.

Aspen. The absolute molecular weight distributions for aspen (experiments A) are shown in Figure 8. The results for A1(t), A1(t + 4), A3(t), and A3(t + 4) are all overlayed in one plot. The amount of lower molecular weight species in A1(t) increased over time, while the amount of the higher molecular weight species decreased as seen in the shift of the distribution, e.g., A1(t + 4). After 2 days of storage, aspen A3(t + 4) was found to have a considerably greater amount of low molecular weight species.

The molecular weight values in Table V show that for the solutions in set A, the molecular weights on the third day were lower than those on the first day. Within the first day, the molecular weight increase was significant. For experiments B, the trends were reversed.

Westvaco Hardwood Kraft. Figure 9 illustrates the molecular weight distributions for the Westvaco HPL's first-day and third-day investigations. In the case of Westvaco A1(t) and A1(t + 4), the distribution has clearly moved to higher molecular weights four hours after sample preparation. On the third day, the distributions indicate an overall decrease of molecular weights upon storage. Sample A3(t + 4) had more low molecular weight species than A3(t). A summary of molecular weight data in Table V shows that for the data in set A, the molecular weights increased on the first day after 4 h and then decreased on the third day. Although the distribution

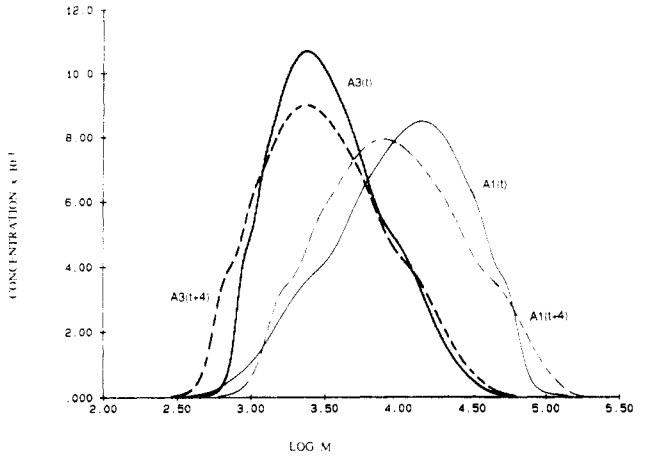

Figure 9. Absolute molecular weight distributions for Westvaco A.

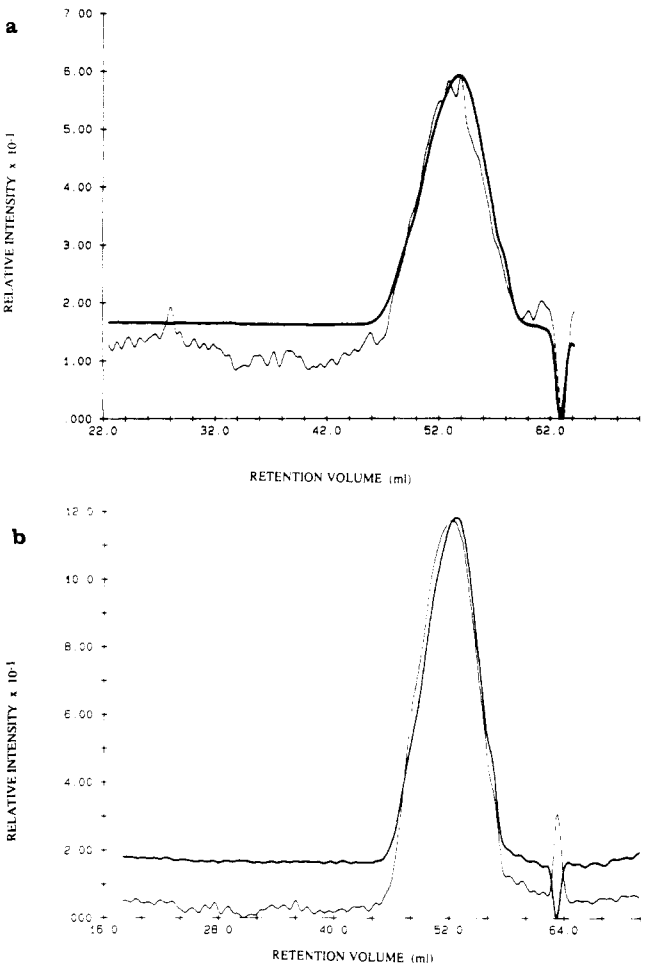

Figure 10. GPC/DV dual chromatogram for (a) red oak B1(t) and (b) red oak with fourfold increase in concentration.

showed more low molecular weight species in the later run on the third day, the average molecular weight did not change greatly.

GPC/DV. Red Oak. An example of the raw data for red oak is shown in Figure 10. Figure 10a is the trace of the data for red oak B3(t). The bold trace represents the DRI signal and the finer trace reveals the concurrent viscosity signal. Again, as was the case of the LALLS, the viscosity detector output was noisier than the DRI signal since the molecular weights of the sample were approaching the DV lower detection limit. Later experiments indicated that the noisy signal may be improved

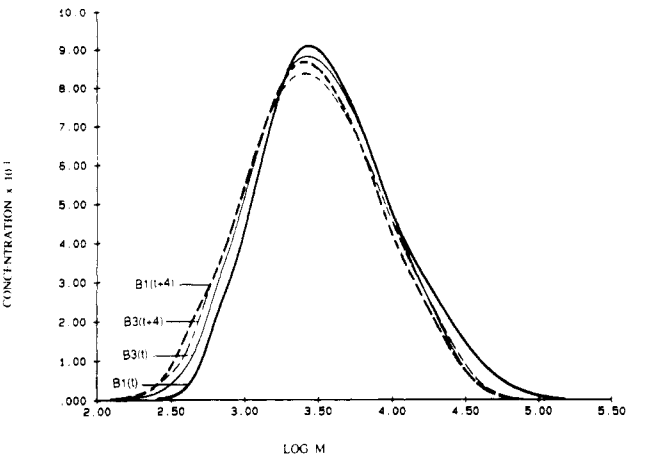

Figure 11. Absolute molecular weight distributions for red oak B.

Table VI
Summary of GPC/DV Results

sample	set	day	time	$[\eta]$, dL/g	$\bar{M}_n$, g/mol	$\bar{M}_w$, g/mol	polydispersity
red oak	A	1	t	0.041	1535	3852	2.51
	B	1	t	0.040	2388	5704	2.39
	A	1	$t+4$	0.039	1732	4109	2.37
	B	1	$t+4$	0.037	1971	4945	2.51
	A	3	t	0.045	1433	4335	3.03
	B	3	t	0.043	2013	5091	2.53
	A	3	$t+4$	0.036	2080	5111	2.46
	B	3	$t+4$	0.041	1676	5045	3.01
RO:PO	A	1	t	0.032	1567	4971	3.17
	B	1	t	0.036	2132	5036	2.36
	A	1	$t+4$	0.045	1367	2741	2.00
	B	1	$t+4$	0.041	1701	3899	2.29
	A	3	t	0.041	1473	3541	2.40
	B	3	t	0.035	1935	5355	2.77
	A	3	$t+4$	0.039	1701	3607	2.12
	B	3	$t+4$	0.038	1628	4752	2.92
aspen	A	1	t	0.044	1591	4783	3.01
	B	1	t	0.045	1889	4825	2.55
	A	1	$t+4$	0.051	1471	3583	2.44
	B	1	$t+4$	0.045	2174	5655	2.60
	A	3	t	0.045	1924	4615	2.40
	B	3	t	0.042	2385	6555	2.75
	A	3	$t+4$	0.047	1846	4630	2.51
	B	3	$t+4$	0.046	1258	3958	3.14
Westvaco	A	1	t	0.047	1597	4589	2.87
	B	1	t	0.043	1515	6254	4.13
	A	1	$t+4$	0.046	1858	6333	3.41
	B	1	$t+4$	0.046	2014	6524	3.24
	A	3	t	0.044	1951	6190	3.17
	B	3	t	0.045	1711	7166	4.19
	A	3	$t+4$	0.048	1518	5580	3.68
	B	3	$t+4$	0.043	897	3982	4.44

by a 4-fold increase in the concentration of the solution used. Such a change in procedure resulted in the much cleaner signal shown in Figure 10b.

The absolute molecular weight distributions for the red oak B1(t), B1(t + 4), B3(t), and B3(t + 4) are overlayed in Figure 11. The distributions of red oak B1(t) and B1(t + 4) appear to form the boundaries for low and high molecular weight materials present. Although the distributions changed in three days as seen in the results for B3(t) and B3(t + 4), the shifts occurred within these boundaries.

A summary of the results from GPC/DV is given in Table VI. For the data set A, the molecular weights increased on the first day, in a span of 4 h. Storage for a couple of days resulted in a slight decrease initially before another increase. For duplicate sample set B, the molecular weights continuously decreased from the first to the third day. It should be emphasized that the DV

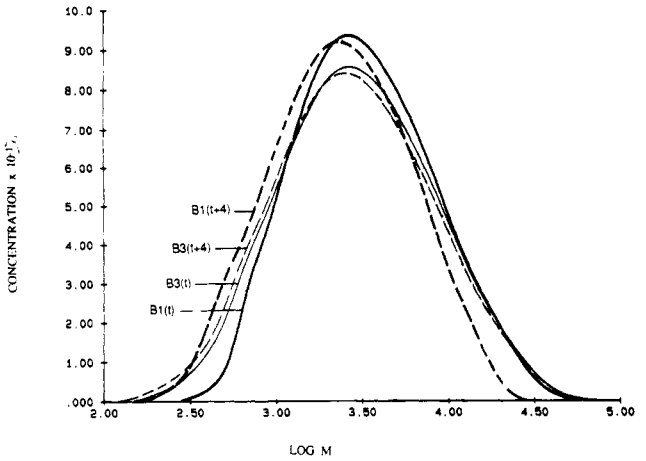

Figure 12. Absolute molecular weight distributions for RO:PO B.

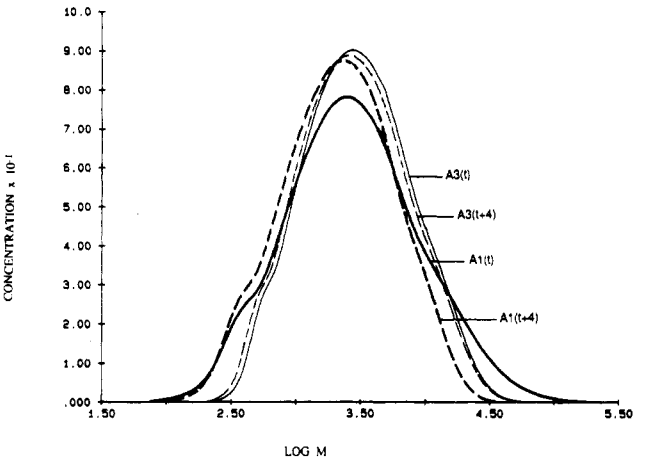

Figure 13. Absolute molecular weight distributions for aspen A.

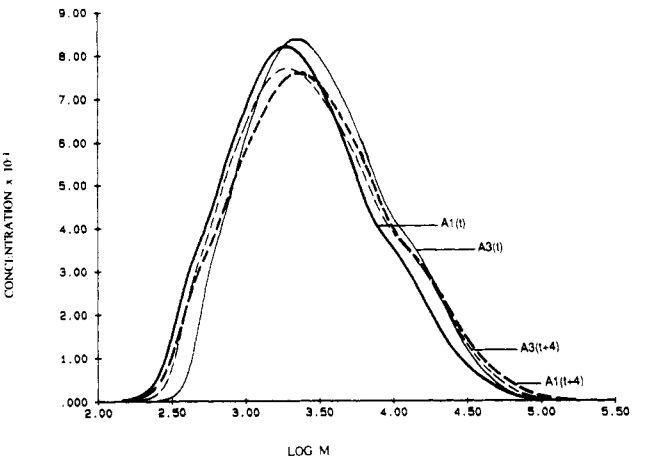

Figure 14. Absolute molecular weight distributions for Westvaco A.

Table VII
Comparison of $\bar{M}_n$ from VPO, GPC/LALLS, and GPC/DV

sample	day	VPO	GPC/LALLS	GPC/DV
red oak	1	1416	6708	1535
	1		9441	2388
	3	1684	1701	1433
	3		4906	2013
RO:PO	1	1108	5433	1567
	1		9326	2132
	3	1348	2459	1473
	3		1578	1935
aspen	1	1393	4004	1591
	1		6470	1889
	3	1691	2205	1924
	3		2190	2385
Westvaco	1	1499	3711	1597
	1		12430	1515
	3	1850	2386	1951
	3		858	1711

results are in substantial agreement with those of the VPO for $\bar{M}_n$ and the changes in $\bar{M}_n$ with time. Furthermore, the noisy signal from the DV did not significantly alter the results obtained. The $\bar{M}_n$ calculated from the improved chromatogram was 1478 g/mol, clearly within error of the values obtained from the noisy DV signal.

RO:PO. The absolute molecular weight distribution for this set of samples is shown in Figure 12. There is an obvious shift toward lower molecular weights after a standing time of 4 h subsequent to the mixing of the sample with the solvent. Again, the shift in the distributions on the first day constitutes the major change. The changes in the distributions for samples B3(t) and B3(t + 4) occur within the high and low molecular weight boundaries set by samples B1(t) and B1(t + 4).

An examination of the results in Table VI reveals that while the values of molecular weights obtained for two sets of identical samples (A, B) were not exactly reproducible, the agreement was certainly satisfactory, in agreement with the VPO, and yielded information on the absolute molecular weight distribution quickly and conveniently.

Aspen. Some of the difficulties in analyzing lignins is once again demonstrated in Figure 13 where the molecular weight distributions for aspen A1(t), A1(t + 4), A3(t), and A3(t + 4) are overlayed. Initially, there was a shift of the distribution to lower molecular weights as shown by solutions A1(t) to A1(t + 4). However, storage for 2 days resulted in an increase in the proportion of high molecular weight species. The distribution then remained relatively constant as evidenced by the almost identical distributions for A3(t) and A3(t + 4).

An examination of Table VI reveals that the molecular weights were between 1500 and 2000 on the first day for the various times that the samples were run. They were generally higher on the third day.

Westvaco Hardwood Kraft. The absolute molecular weight distributions for set B of samples is shown in Figure 14. The molecular weights clearly increased within 4 h of sample preparation as seen from the shift in distribution from Westvaco A1(t) to A1(t + 4). After storage for a couple of days, the distributions did not seem to be altered significantly from its state in A3(t) to A3(t + 4).

A look at the results in Table VI reveals that for this sample, the trends, as well as the values of molecular weights were reproducible between experiments A and B and were supported by the VPO analyses.

GPC/DV/LALLS. A summary of the results from the GPC and VPO are given in Table VII. The values of number-average molecular weights chosen for comparison were those obtained immediately after initial sample preparation since this is the state of the solutions for the VPO experiment. If the $\bar{M}_n$ obtained by VPO were used as the "correct" value, then the contents of Table VII suggest that GPC/DV yielded results that were consistently closer to this number than did those from GPC/LALLS. The LALLS detector generally produced higher values. This indicates that there was a need to do the LALLS experiment with the beam polarization correction which reportedly brings the numerical values down

by 30–40%.

Summary and Conclusions

The work presented above has shown that VPO can be used to very reliably obtain number-average molecular weights for the HPL lignin derivatives if a multiple standard calibration scheme is employed. In addition, a time study revealed that number-average molecular weights by VPO increased over time as a result of association.

Results obtained by GPC showed that in order to use the LALLS detector, one has to consider not only the influence of sample absorbance and fluorescence on molecular weight determination but also the effect of beam polarization. Without the polarizer correction (which requires 0° and 90° measurements), the LALLS gave erroneously high molecular weights when compared to the VPO. Furthermore, static LALLS measurements were complicated by association which brought about irreproducible surges in scattered intensity. This lack of consistency did not permit the calculation of second virial coefficients from LALLS. The VPO proved to be a valuable source of the second virial coefficient for the GPC/LALLS calculations.

The results obtained by GPC/DV proved that the viscosity detector is a quite acceptable and convenient instrument for obtaining absolute molecular weights and molecular weight distributions for these polydisperse low molecular weight HPL lignin derivatives. Inspite of some noise in the raw data that were a consequence of signals close to the lower detection limit of the detector, very good results were obtained. This strongly indicates that the lignins studied could be analyzed by a universal calibration GPC procedure. Hence, the viscosity detector provides a means of obtaining absolute molecular weights and molecular weight distributions reliably, quickly and easily.

The changes in absolute molecular weight distributions obtained here in *all* experiments confirm that a time-dependent association does occur in lignin derivatives. In addition, there was positive evidence for McCarthy's postulate that association in lignins occurs by the specific interaction between high and low molecular weight species. This was illustrated by the shift of the molecular weight distribution toward higher molecular weights over time as the smaller species are "consumed" through association to form larger molecules.

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Registry No. Hydroxypropyl organosolv lignin, 88402-80-6; hydroxypropyl kraft lignin, 88402-77-1.

Morphological Arrangements of Block Copolymers That Result in Low Gas Permeability

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ABSTRACT: Gas permeability coefficients for several gases (Ar, N_2, CO_2, CH_4) were measured at 25 °C in two polystyrene/polybutadiene block copolymer systems. One possesses a morphology of alternating lamellae that are highly oriented and perpendicular to the permeation direction; the second contains spheres of polybutadiene in a polystyrene matrix. The measured permeabilities of these two materials are dominated by the behavior of the low permeability polystyrene component. Models are presented to describe transport in these microphase-separated systems and to facilitate comparisons with the transport behavior of other two-component polymer systems.

Introduction

The use of polymers in applications that require control of gas transport is increasing rapidly.[1,2] Prominent examples include polymer membranes for gas separations, where low-energy requirements make such processes extremely attractive to industry, and plastic containers and packages, which are currently being used to hold items from foodstuffs to industrial solvents. For many applications, it may be desirable to utilize heterogeneous polymer blends or block copolymers in which one component provides desired permeability characteristics, while the other improves material properties such as modulus or impact strength. If the final application requires that a low-permeability component provide a barrier quality or an enhanced selectivity, it will be desirable (and probably necessary) to have the individual components of the heterogeneous material arranged in series with respect to the permeation direction. In this manner, the diffusing species will not be able to circumvent the low permeability phase via high-conductivity pathways.

In previous investigations from this laboratory[3,4] on the gas permeability of a polystyrene/polybutadiene block copolymer with a lamellar morphology, alternating lamellae of polystyrene and polybutadiene were either misordered[3] or aligned in parallel with the permeation direction.[4] Here we report the behavior of two polystyrene/polybutadiene block copolymer samples whose morphological arrangements allow the low-permeability polystyrene to exert a greater influence on the overall transport properties, causing them to be considerably less permeable than these earlier cases. One is a lamellar system in which the platelike microdomains are oriented in the same plane as the film surface, in series with respect to permeation. The second system exhibits a morphology of discrete polybutadiene spheres contained in a polystyrene matrix.

Experimental Section

The lamellar block copolymer used in this investigation was the same K-Resin polymer used previously.[4] This material contains 75% by volume polystyrene; detailed characterizations have been described earlier.[4] In order to obtain sample films in which lamellae exist parallel to the film surface, the material was exposed to a melt flow technique similar to those employed by earlier investigators[5,6] to yield highly ordered block copolymer morphologies. Well-controlled solvent-casting techniques have also been described, which result in thin block copolymer films that possess alignment parallel to the film surface,[7,8] but these were not employed here.

The production of ordered lamellar films consisted of a two-stage process. First, films of 1.6-mm thickness were made by compression molding in a hot press at 160 °C. Morphological characterization of the resulting 5 × 5 cm square films using small-angle X-ray scattering (SAXS) indicated that there was some lamellar orientation near the film perimeter. However, considerably poorer alignment existed near the center of these samples, where presumably less flow occurred during the first-stage molding procedure. The second step consisted of squeezing the molded film between two parallel Teflon-coated steel plates (of the same surface dimensions as the molded film), again at 160 °C, to a final thickness of 0.25 mm (compression ratio ≈ 6). The gap between the plates was closed at a rate of approximately 0.3 mm/s. As opposed to being confined by a mold, during this compression step excess material was permitted to flow out from between the plates. Two-dimensional SAXS patterns from these squeezed samples with the beam parallel to the film surface (Figure 1a) show first- and second-order maxima, which indicate excellent long-range microphase orientation parallel to the film surface in regions both near the film perimeter as well as near its center. The virtual absence of scattering when the incident beam is perpendicular to the film surface (Figure 1b) lends strong support to the view that the platelike lamellar domains are indeed aligned with the plane of the film. Transmission electron microscopy (TEM) of osmium-stained thin sections from these films also indicates long-range lamellar orientation parallel to the film surface (Figure 2). It is concluded that a permeating species will encounter polybutadiene and polystyrene lamellae in series in these films, and

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