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Lignin. XVII. Preparation and Characterization of Acetyl Lignin Sulfonate Methyl Esters[a]

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ABSTRACT: Lignin sulfonates obtained through sulfonation of Western Hemlock wood chips (W), and also lignin sulfonates prepared from milled wood lignin (MWL), were fractionated by Sephadex gel chromatography in aqueous solution and then acetylated and methylated. The resulting acetyl lignin sulfonate methyl ester (ALSME) fractions were characterized by nuclear magnetic resonance spectroscopy carried out in deuteriochloroform solutions, and the usefulness of this procedure was established. The ALSME-MWL fractions were also characterized by chemical analyses. Mass spectroscopy did not yield useful results. The findings are interpreted in relation to the structure of lignin sulfonates. Gel permeation chromatography of ALSME fractions was carried out in methanol on Sephadex LH-20 and yielded further evidence indicating the separation in part of low molecular weight ALSME species including one which was obtained in crystalline form.

New knowledge of the structure of lignin polymers can be approached by study of their sulfonate derivatives. Thus investigations of the separation, purification, and characterization of lignin sulfonate (LS) preparations have been going forward for several years in this laboratory,[3] in Helsinki, and elsewhere,[4–7] and recently these and related endeavors have been reviewed.[8] Gel chromatography has been shown to give rather effective fractionation of LS on a molecular weight and size basis.

In recent work in this laboratory, certain LS-like monomeric and dimeric compounds have been converted to organic solvent-soluble derivatives.[9] The phenolic and aliphatic hydroxyl groups were first acetylated and then, using a modification of a procedure described by Gellerstedt and Gierer,[10] the sulfonate groups were converted to methyl esters. These derivatives were examined by NMR and mass spectroscopy procedures.

In the present investigation, it was desired to learn how to convert lignin sulfonates themselves to organic solvent-soluble derivatives, and preferably to acetylated methyl sulfonate esters, which could be investigated by NMR and mass spectroscopy and by other techniques. While this work was being prepared for publication, a related paper by Gellerstedt and Gierer[11] dealing with model substances has appeared. It has now been found that LS fractions of varying molecular weights derived directly from Western Hemlock wood (W),[12] and also milled wood lignin (MWL) isolated according to Bjorkman's procedure[13–15] by grinding wood for an extended period of time and extracting lignin with dioxane, can be converted to acetylated lignin sulfonate methyl ester (ALSME) derivatives. These substances, when dissolved in appropriate nonpolar solvents, yield significant nuclear magnetic resonance (NMR) spectra. The MWL preparations have been characterized also by chemical analyses. Lignin sulfonates derived from MWL were studied because the literature indicates that MWL is very similar structurally to at least a substantial part of the lignin of wood, and also is substantially free from carbohydrate and extractive components.[13–15]

Experimental Section

Preparation of Fractions. LS-W. Western Hemlock (Tsuga Heterophylla) wood was delignified by use of an aqueous solution of sulfur dioxide and calcium oxide under mild conditions, as previously described.[12] The resultant LS-containing solution was partially purified from sugars and carbohydrate type substances by column chromatography using a Dowex 50-2W resin. It was then fractionated by column chromatography using a Sephadex G-25 gel to yield an elution pattern which was similar to the pattern shown in Figure 1.

LS-MWL. MWL[13] prepared from Western Hemlock wood was converted to LS by treating with a solution of $NaHSO_3$ and SO_2 at 100°C for 24 hr, as previously described.[12] Degassing of the resultant yellow solution, concentrating, and then converting to barium salts resulted in the removal of excess SO_2 and sulfate ions. The barium salts of the sulfonates were transformed into calcium salts by cation exchange on Dowex 50W-X8, 50–100 mesh, Ca^{2+}; then this solution was fractionated by Sephadex G-25 gel chromatography. Elution pattern results from 280 nm absorption measurements are plotted in Figure 1. Certain cuts were combined, concentrated, and freeze dried to yield 12 fractions (see Figure 1), and each contained 100–150 mg of dry solids. Yields and other information pertinent to these fractions are listed in Tables I–V. A total of 2.42 g (vacuum dried over P_2O_5) of LS-MWL was recovered

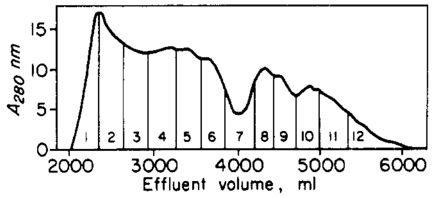

Figure 1. Elution pattern for Sephadex G-25 gel chromatography for LS-MWL and showing fraction numbers.

Table I
Yields in Preparation of ALSME-MWL from CaLS

Fraction[a]	Initial CaLS, mg	Acetylated[b] CaLS-EIS, mg	ALSME, mg	ALSME[b] EIS, mg	ALSME-EIS of CaLS, %
1	197	223	176	152	77
2	283	361	163[c]	143	51
3	320	381	289	274	86
4	312	404	329	312	100
5	268	424	260	225	84
6	216	293	238	192	89
7	176	225	152	93	53
8	207	275	216	141	68
9	148	187	118[c]	69	47
10	127	165	121	79	62
11	101	128	86	39	39
12	69	79	43	28	41
Total	2424	3145	2191	1747	72

[a] Origin identified in Figure 1. [b] EIS = ether insoluble. [c] Some losses by spillage.

Table II
Results of Chemical and NMR Analyses of ALSME-MWL Fractions[a,b]

Fraction	C	H	S	OCH_3	$OCCH_3$[c]
MWL	61.73*	5.84*		15.08*	
1	55.97*	5.26*	4.06	12.14	18.6(24.9)
2	56.00*	5.30*	4.58	13.07	15.1(20.0)
3	55.04*	5.35*	5.37*	12.05*	18.0(23.7)
4	54.72*	5.28*	5.64	14.06	17.6(23.5)
5	54.44*	5.21*	5.56	12.78	19.0(25.7)
6	54.10*	5.29*	5.57	13.38	19.0(25.3)
7	54.37*	5.31*	5.88*	12.96*	19.0(25.7)
8	54.57*	5.18*	5.36	12.89	17.7(24.1)
9	54.60*	5.16*	5.32	12.38	19.9(27.1)
10	54.88*	5.35*	4.82*	11.08*	21.0(27.6)
11	55.92*	5.28*	4.56	11.04	21.5(28.7)
12	55.44*	5.36*	4.03	8.92	23.9(31.3)

[a] Weight percent of dry ALSME. [b] All numbers with asterisks constitute mean values from duplicate determinations of C, H, S, and OCH_3 by chemical methods. [c] Acetyl was determined by use of an NMR spectroscopic method. The numbers within the parentheses are the percentages of total protons which are acetyl protons (see Table IV).

from the Sephadex, e.g., about 90% of the theoretical weight yield, assuming 0.35 sulfonate group per C_9 unit.

Estimation of Molecular Weights of LS Fractions. The average molecular weights, $\bar{M}$, of the LS molecules in the several W and also MWL fractions studied in the present work were estimated from the relative elution volumes (V/V_0) where V and V_0 signify the volume of eluant collected up to the midpoint of the sample of interest, and the void volume of the column, respectively.

Table III
Certain Atoms and Functional Groups in ALSME-MWL Fractions (per Nine Carbon Atoms Excluding Acetyl and Methoxyl Carbon)

MWL fraction no.	No. of atoms and functional groups						Structural unit wt[a]	Total protons
	C	H	O	$-COCH_3$	$-OCH_3$	$-SO_3H$		
1	9	7.03	2.64	1.14	1.03	0.34	268, 263	13.54
2	9	7.27	2.31	0.89	1.07	0.36	254, 252	13.15
3	9	7.38	2.26	1.12	1.04	0.46	268, 274	14.46
4	9	7.07	2.38	1.12	1.23	0.49	272, 278	14.12
5	9	7.00	2.42	1.23	1.14	0.47	277, 270	14.11
6	9	7.21	2.93	1.24	1.21	0.48	280, 276	14.66
7	9	6.92	2.46	1.23	1.17	0.50	280, 272	14.12
8	9	6.99	2.52	1.12	1.14	0.46	274, 274	13.77
9	9	6.77	2.48	1.29	1.12	0.48	280, 288	14.00
10	9	7.33	2.53	1.36	1.00	0.42	280, 278	14.41
11	9	6.99	2.37	1.36	0.98	0.38	274, 266	14.01
12	9	7.44	2.79	1.55	(0.81)[b]	0.36	281, 286	14.52

[a] The ALSME structural unit weights have been calculated and are presented based on methoxyl and also sulfur determinations, respectively. [b] Total by chemical analysis.

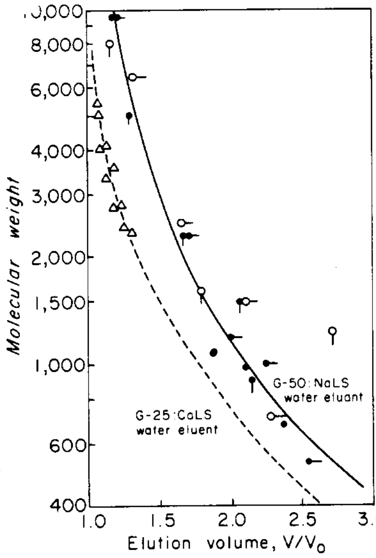

Figure 2. Relation between Sephadex elution volume and molecular weight for lignin sulfonates: △, cases A and B, Stenlund;[16] ○- and ♀, series A, 0.0001 and 0.001 M NaCl, Gupta;[3] ●, ●-, and ⧭, series A water, 0.0001 and 0.001 M NaCl, Gupta.[3]

In prior work in this laboratory,[3] the average molecular weights were determined by sedimentation equilibrium of the sodium lignin sulfonate (NaLS) fractions collected at several relative elution volumes using Sephadex G-50 with water or aqueous 0.0001 M NaCl or 0.001 M NaCl as the eluant, and these data are plotted in Figure 2.

In present experiments, the calcium lignin sulfonates (CaLS) were fractionated using Sephadex gel G-25 with water as the eluant (Figure 1) and the several relative elution volumes were measured (Table V).

Estimation of average molecular weights of CaLS fractions was greatly assisted by experimental data kindly provided by Dr. Bengt Stenlund[16] of the Finnish Pulp and Paper Research Institute at Helsinki, Finland, who fractionated certain lignin sulfonate samples, estimated $\bar{M}$ by light scattering experiments, and obtained the results in Chart I.

For the lower molecular weight CaLS molecules of present interest, the relationship between molecular weight and V/V_0 was taken to be similar to that found in our prior work for NaLS, as is represented by the dotted line shown in Figure 2, and the so esti-

Table IV
NMR Signals for ALSME-MWL Fractions

	Aromatic H			Aliphatic and methoxyl H	Acetyl H		
Fraction	Ortho to α carbonyls and β ethers 2.00–2.75[a]	Others 2.75–3.72	Total 2.00–3.72	Total 3.72–7.50	Phenolic 7.50–7.81	Aliphatic 7.81–8.42	Highly shielded H 8.42–9.20
			ALSME-MWL Fractions				
1	3.7[b]	11.8	15.5	55.6	5.5	19.4	4.0
	0.51[c]	1.6	2.1	7.7	0.76	2.7	0.55
2	3.8	15.2	19.0	58.6	4.9	15.1	2.4
	0.51	2.0	2.5	7.8	0.66	2.0	0.32
3	4.0	13.7	17.7	57.1	5.3	18.4	1.4
	0.57	2.0	2.5	8.1	0.76	2.6	0.20
4	3.5	13.9	17.4	57.4	5.8	17.7	1.6
	0.50	2.0	2.5	8.3	0.84	2.6	0.23
5	2.9	12.9	15.8	57.3	6.3	19.4	1.2
	0.42	1.9	2.3	8.3	0.91	2.8	0.17
6	3.5	13.7	17.2	56.4	6.7	18.6	1.2
	0.52	2.0	2.5	8.3	0.99	2.8	0.18
7	3.9	14.1	18.0	54.2	7.0	18.7	2.2
	0.56	2.0	2.6	7.8	1.0	2.7	0.32
8	4.3	12.6	16.9	57.0	6.7	17.4	2.0
	0.60	1.8	2.4	8.0	0.94	2.4	0.28
9	3.1	13.7	16.8	54.0	7.6	19.5	2.1
	0.44	2.0	2.4	7.7	1.1	2.8	0.30
10	4.9	14.8	19.7	50.5	8.1	19.5	2.2
	0.73	2.2	2.9	7.5	1.2	2.9	0.33
11	4.2	13.6	17.8	53.3	10.0	18.7	.0
	0.60	1.9	2.5	7.6	1.4	2.7	.0
12	2.9	11.5	14.4		12.4	18.9	3.1
	0.43	1.7	2.1		1.8	2.8	0.46

[a] Range of τ values. [b] Upper line: % of total integration. [c] Lower line: number of H of 14 H per C_9 unit.

Chart I
Elution Behavior of Calcium Lignin Sulfonate Fractions on Sephadex G-25 (Fine) with Water as Eluant

$\overline{M}$	V, ml	V/V_0
Case A (degree of sulfonation of LS = 1.9–2.4 mequiv/g; V_0 = 6850 ml)		
5060	7247	1.057
4080	7500	1.094
3340	7795	1.137
2820	8154	1.190
2470	8554	1.249
Case B (degree of sulfonation of LS = 2.4–2.7 mequiv/g; V_0 = 6775 ml)		
5310	7293	1.076
4150	7641	1.127
3590	7953	1.173
2850	8435	1.245
2350	8786	1.296

mated average molecular weights of the LS samples are shown in Table V.

Preparation of ALSME Derivatives. The several LS-W fractions were freeze dried and swollen in water and then excess pyridine was added. The lower boiling pyridine–water azeotrope was removed by vacuum evaporation at room temperature. Acetic anhydride was added, whereupon the LS stayed completely in solution which did not occur when the conventional acetylation procedure was used. After standing for 24 hours at room temperature, the solvents were removed by vacuum evaporation to yield the acetylated product.

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The CaLS acetates were dissolved in water and the free acids were prepared by running the solution through a column filled with Dowex 50W-X8 resin in H^+ form. This solution was neutralized with silver oxide, filtered, freeze dried, dissolved in acetonitrile, and then reacted with an excess of methyl iodide for 24 hr at room temperature. At all times when silver salts were present, light was excluded to avoid decomposition. After removal of silver iodide by filtration, the filtrate was vacuum evaporated to yield the cream-colored amorphous ALSME-W.

Some preparations of apparently higher purity were made using a milder procedure: an aqueous solution of free LS-W acids was passed through a column filled with Dowex 50W-X8 in Ag form. The resultant solution of silver salts was treated as already described.

The ALSME-MWL materials were prepared as just described except that the CaLS salts were purified by precipitation from ethanol solution by adding the latter to 15 volumes of ether. The ether-insoluble acetates were converted into ALSME-MWL derivatives which were dissolved in chloroform to make about 5% solutions, and these were added to about 15 volumes of ether to precipitate the ALSME-MWL fractions. The precipitates were vacuum dried over P_2O_5 and parafin and yields are shown in Table I.

Elemental Analyses. Elemental analyses of the ALSME-MWL fractions for C, H, OCH_3, and S were carried out by Alfred Bernhardt, Mikroanalytisches Laboratorium, Elbach, West Germany, and the results are given in Tables II and III.

NMR Spectroscopy. The NMR spectra of ALSME fractions were recorded using a Varian A-60 instrument, with samples of about 60 mg dissolved in 0.4 ml of $DCCl_3$.[9] To illustrate the type of

Table V
Lignin Sulfonic Acid Characteristics from ALSME-MWL Data (per C_9 Unit)

Fraction no.	GPC elution V/V_0	$\bar{M}$	$\bar{n}$[a]	Unallocated		Aromatic				Aliphatic			Structural unit wt
				$(H)_a$	$(O)_b$	$(H)_c$	$(OH)_d$	$(OCH_3)_e$	$(-O-)_f$	$(H)_h$	$(OH)_i$	$(SO_3H)_j$	
1	1.03	7100	32.3	0.33	0.69	2.10	0.25	0.94	0.81	4.6	0.89	0.34 (0.09)[b]	217
2	1.11	4400	20.0	0.17	0.58	2.50	0.22	0.94	0.84	4.6	0.67	0.36 (0.13)	213
3	1.30	2400	10.9	0.28	0.31	2.50	0.25	0.94	0.81	4.6	0.89	0.46 (0.10)	221
4	1.45	1700	7.8	−0.03	0.47	2.50	0.28	0.94	0.78	4.6	0.85	0.49 (0.29)	227
5	1.58	1300	5.9	−0.20	0.43	2.30	0.30	0.94	0.76	4.9	0.93	0.47 (0.20)	223
6	1.72	1000	4.6	−0.19	0.45	2.50	0.33	0.94	0.73	4.9	0.92	0.48 (0.27)	227
7	1.86	850	3.9	0.07	0.50	2.60	0.34	0.94	0.72	4.3	0.90	0.50 (0.23)	229
8	2.00	720	3.3	−0.01	0.65	2.40	0.31	0.94	0.75	4.6	0.81	0.46 (0.20)	226
9	2.14	650	3.0	−0.23	0.49	2.40	0.36	0.94	0.70	4.6	0.93	0.48 (0.18)	227
10	2.24	560	2.5	−0.07	0.51	2.90	0.40	0.94	0.66	4.5	0.96	0.42 (0.06)	221
11	2.42	470	2.1	−0.26	0.42	2.50	0.48	0.94	0.58	4.7	0.89	0.38 (0.04)	215
12	2.65	400	1.8	0.64	0.74	2.10	0.61	0.94	0.45	4.7	0.94	0.36 (0)	220

[a] Assuming the SU weight = 220. [b] The first number shown is the total sulfonate. The number in parentheses is the percentage of sulfonate methyl ester estimated to have been present in the ALSME-MWL fraction.

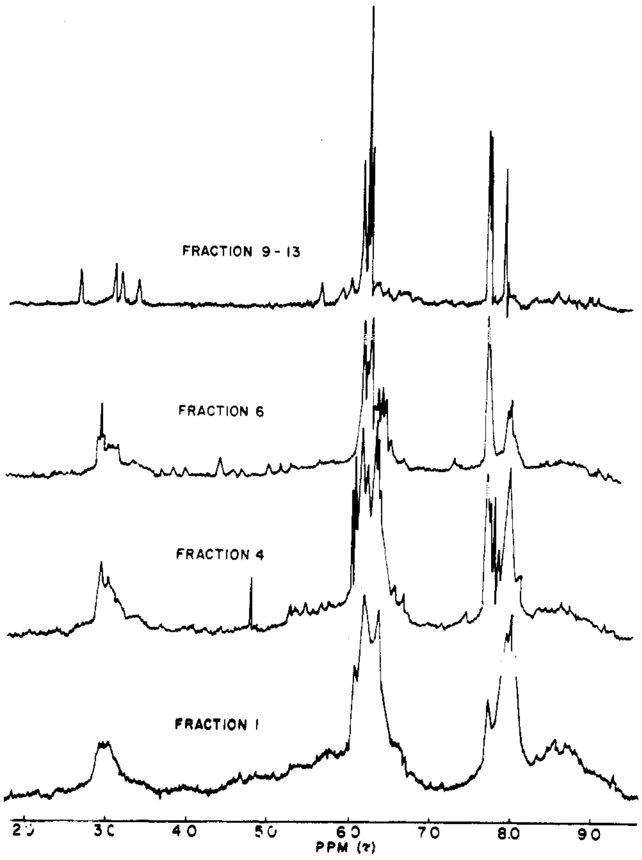

Figure 3. NMR spectra of four selected ALSME-W fractions.

NMR spectra obtained, results for certain ALSME-W and ALSME-MWL fractions are given in Figures 3, 4, and 5, respectively. The spectra were divided into frequency ranges,[9,17–20] and the resultant relative distributions of protons in various regions for the several fractions are set forth in Table IV for the MLW fractions.

Mass Spectrography. In view of the effectiveness of mass spectroscopic procedures in providing for the characterization of LS-like monomeric and dimeric derivatives, as we have reported in a prior paper,[9] this technique was applied to low molecular weight ALSME-W fractions, but useful results were not obtained, apparently because the mixtures of compounds within the fractions were too complex to yield interpretable signals.

Sephadex LH20 Fractionation. For analytical purposes, a column (1.9 cm diameter; 114 cm bed height; 75.3 g gel wt) was prepared using Sephadex LH 20. ALSME samples (5 mg) were dissolved in 9.2 ml of methanol and applied to the column. Flow was held constant at about 0.2 ml cm^{-2} min^{-1}, and the uv absorption spectra of the eluant solution was monitored continuously at 280 nm. For preparative purposes, similar arrangements were used (column 5.0 cm diameter, 195 cm bed height, and 920 g gel wt) with ALSME samples of 200–300 mg.

Thin Layer Chromatography (TLC). The several ALSME-W fractions were examined using precoated silica gel HF_{254} plates, 0.25 nm layers (Merck) with 1:1 benzene–ethyl acetate serving as the developer. Concentration spots were observed by using ultraviolet illumination which yields fluorescence, or by spraying with 50% H_2SO_4 and heating (105°C). On an analytical scale, the lower molecular weight ALSME-W fractions showed the presence of two or three major constituents accompanied by other compounds. By preparative TLC no compounds could be isolated apparently because of the instability of these ALSME-W derivatives on prolonged contact with silica gel.

Results and Discussion

The LS-W fractions originating from Western Hemlock wood were separated by Sephadex G-25 gel chromatography. With MWL, sulfonation was first carried out, and the resulting LS-MWL preparation then was similarly fractionated and an illustrative pattern is shown in Figure 1. For estimation of molecular weights, use was made of the relationship shown for CaLS fractions in Figure 2.

Considerable attention was devoted to the development of effective procedures by which LS preparations could be converted to ALSME derivatives. Preliminary experiments using the usual pyridine–acetic anhydride method yielded incomplete acetylation, apparently because of incomplete solubility of the higher molecular weight LS in the acetylation mixture. Satisfactory acetylation was finally accomplished after inauguration of a preliminary step consisting of freeze drying and then reswelling the LS. The methyl esters were prepared through the silver salt using the method which we have previously used with LS-like model substances[9] and similar to a method described by Gierer.[10,11] These procedures satisfactorily provided for the preparation in about 80% weight yield (Table I) of ALSME derivatives of unfractionated LS, and also of the several LS fractions. The ALSME perparations, as expected, were found to be soluble in organic solvents.

Chemical Analyses. The elemental analyses of the several ALSME-MWL fractions were determined, and the results are shown in Table II.

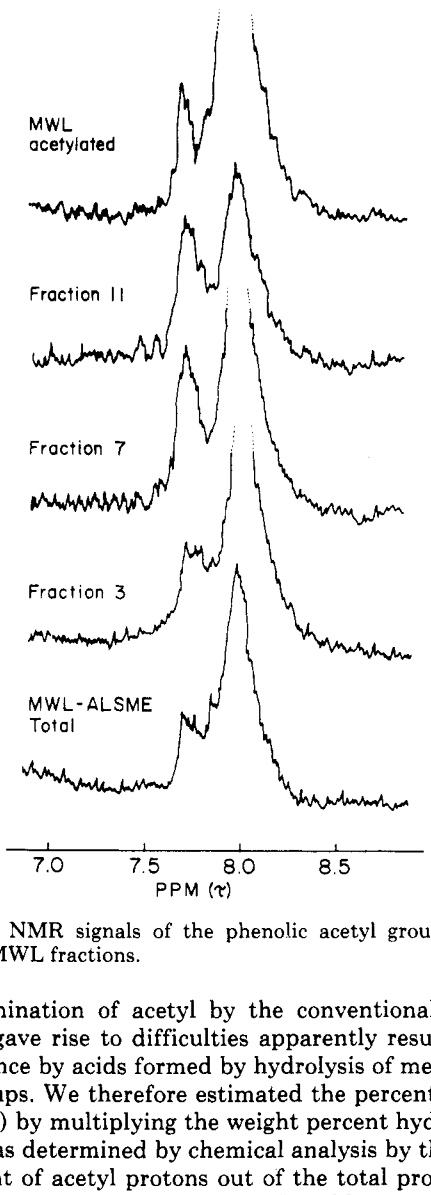

Figure 4. NMR signals of the phenolic acetyl groups of some ALSME-MWL fractions.

Determination of acetyl by the conventional chemical method gave rise to difficulties apparently resulting from interference by acids formed by hydrolysis of methyl sulfonate groups. We therefore estimated the percentage acetyl (Table II) by multiplying the weight percent hydrogen in a fraction as determined by chemical analysis by the number of percent of acetyl protons out of the total protons of all types indicated by NMR (Table IV) and by 43.044 (the formula weight of $COCH_3$), and then dividing by three times 1.008 (the formula weight of H) and by 100.

From these data, the numbers of certain atoms and functional groups present in each of the 12 ALSME-MWL samples were calculated relative to a presumed phenyl–propane skeletal structure for the polymer (Figure 6), and results are shown in Table III along with the structural unit weights and the total number of protons present per C_9 unit.

The structural unit weights for the several fractions range around 270 and turn out to be slightly different when calculated from total methoxyl vs. total sulfur analyses.

NMR Spectroscopy. In several prior studies in this laboratory and elsewhere,[17-20] NMR spectroscopy has provided significant information concerning lignins, although our earlier attempts to examine LS preparations dissolved in heavy water did not give useful NMR spectra.[21] In the present work, however, it was found that the ALSME-W and ALSME-MWL fractions dissolved in deuteriochloroform gave well-resolved NMR spectra over considerable range of molecular weights (Figures 3, 4, and 5). Thus it appears that by converting the LS polar groupings to esters, the presumed hydrogen bonds affecting the proton signals were reduced or eliminated so that useful results were obtained.

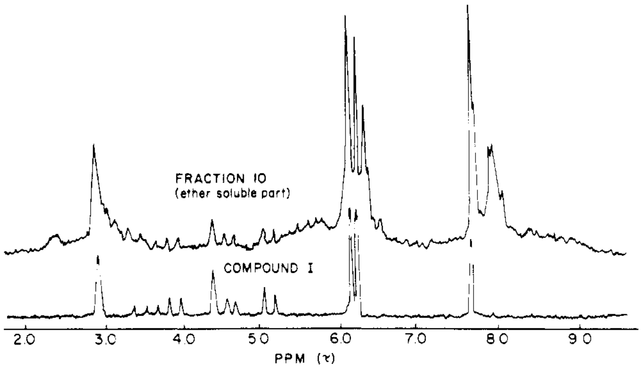

Figure 5. NMR spectrum: Eugenol structures in fraction 10 of ALSME-MWL and in model compound I.

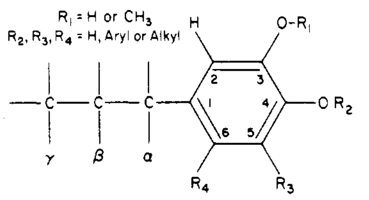

Figure 6. Lignin structural unit of phenyl propane type.

For the several ALSME-MWL fractions, the NMR spectroscopy results are shown in Table IV on two different bases. In the first rows, results are given as percentages of the total integrated proton signals observed between the two boundaries of τ associated with protons in each of certain characteristic structural situations. In the second rows, results are given in terms of the numbers of the protons presumed to be associated with atoms and functional groups in certain structural locations per C_9 structural unit in the ALSME polymer, and corresponding to certain ranges of τ signals.

For the several ALSME-MWL fractions, the total number of protons present was found to be about 14/C_9 unit (Table III), and evidence supporting the presence of approximately this number has been published by Lenz[19] in confirmation of our earlier findings.[17] Thus, for the ALSME-W fractions, in the absence of elemental analyses it was assumed that the integrated proton signal for each fraction reflects the presence of 14 protons per C_9 polymer structural unit.

τ value ranges have been assigned to protons associated with certain functional groupings in most cases in the same way as reported previously,[9,17,20] and these ranges are indicated in Table IV. Functional groups considered are the following: aromatic protons ortho to α carbonyls and α sulfonated β ethers, other aromatic protons, aliphatic protons, ether and ester methoxyl protons, phenolic acetyl protons, aliphatic acetyl protons, and highly shielded protons.

We recognize that caution must be exercised in interpreting at least some ranges of τ values in NMR spectra in terms of frequency of occurrence of functional groups since considerable overlapping occurs with the signals associated with certain protons, such as methoxyl and aliphatic hydrogen. Moreover the fractions studied are doubtless mixtures of a number of substances, and thus an observed signal will be a summation of the contribution of the protons of the component molecules and will tend to be difficult to interpret stoichiometrically. However, the ALSME-MWL fraction 10 exhibited NMR signals (Figure 5) which were similar to those manifested by 1-guaiacyl-2-propene sulfonate, a compound isolated previously in this laboratory and elsewhere from wood delignification[22-26] and from coniferyl alcohol sulfonation[27] reaction mixtures.

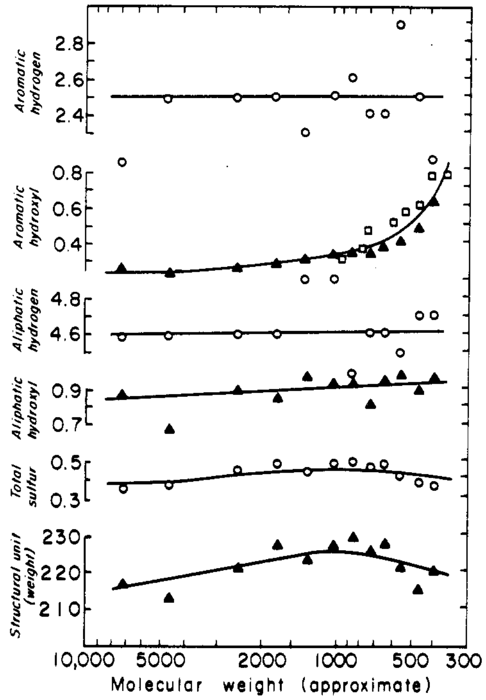

Figure 7. Some lignin sulfonic acid characteristic per C_9 vs. molecular weight: ○ and ▲, ALSME-MWL; and □, ALSME-W fractions.

Functional Groupings. For the several ALSME-MWL fractions, using the above-described chemical and NMR spectroscopy findings along with certain concepts described below, approximate values have been determined for the coefficients associated with certain atoms and functional groupings for the lignin sulfonates in terms of the basic phenylpropane skeletal structure presumed for this polymer (Figure 6), as suggested in the following formulation:

$$C_9H_aO_b[(H)_c(OH)_d(OCH_3)_e(\text{-O-})_f(\text{—})_g]_{\text{aromatic}} \cdot [(H)_h(\text{-OH})_i(\text{—})_j(\text{—})_k(SO_3H)_l]_{\text{aliphatic}}$$

and summarized in Table V. In Figure 7, the results are plotted against estimated molecular weights. Insofar as available data permitted, similar calculations were made for the ALSME-W fractions.

The several coefficients are represented by lower case letters, the presumed aromatic and aliphatic bound atoms and groupings are bracketed, and certain groupings or linkages are defined as follows: $(\text{-O-})_f$ = aromatic ether linkages; $(\text{—})_g$ = aromatic carbon linkages; $(\text{—})_j$ = aliphatic ether linkages; $(\text{—})_k$ = aliphatic carbon linkages; and $(SO_3H)_l$ = total sulfonic acid grouping. The procedures used for the estimation of these coefficients will now be described.

In earlier work,[17,19] it was established that phenolic acetyl protons (τ = 7.50–7.81) can be determined with good precision by use of NMR spectroscopy. Thus the phenolic acetyl (Table IV) and the corresponding *phenolic hydroxyl* groupings (coefficient *d*) have been calculated from NMR observations. The results for both the MWL and the W preparations are plotted in Figure 7, and are in approximate agreement. Similar phenolic hydroxyl values reported elsewhere[12] were obtained for the same LS-MWL fractions using the ultraviolet absorption method of Goldschmid et al.[28]

Aliphatic acetyl groupings, corresponding to *aliphatic hydroxyl* configurations in the LS fractions prior to acetylation, are indicated by NMR (τ = 7.81–8.42) to be present to the extent of about 0.9 per C_9 unit with considerable scattering (coefficient *i*). Highly shielded protons (τ = 8.42–9.20) are observed in small proportion.

From NMR evidence (τ = 2.00–3.27), *aromatic protons* (coefficient *c*) are indicated to be present to the extent of about 2.4 H per C_9 unit. Some protons of this type (τ = 2.00–2.75) are indicated to be situated ortho to α carbonyl and α sulfonate β ether configurations.

In our prior studies on ALSME-like monomeric and dimeric compounds, it was found that the range of the signals associated with *aliphatic protons* and methoxy protons is about τ = 3.72–7.50 with considerable overlapping and thus the total signal in this range was computed (Table IV).

To estimate *total methoxyl groupings*, we have placed reliance on the results of chemical analysis (Tables II and III), which indicates the presence of about 1.1 OCH_3 per C_9 as the total of the aromatic methoxyl and the methyl ester sulfonate configurations. On this basis, we have calculated the number of *total aliphatic protons* (coefficient *h*) subtracting from the signal in the range τ = 3.72–7.50 the signal expected to arise from the methoxy protons determined by chemical analysis, e.g., for ALSME-MWL fraction 8, total aliphatic H = 8.0 − 3(1.14) = 4.6.

The *total sulfur* determined by chemical analysis to be present in the ALSME-MWL fractions (Table II) was considered as a first approximation to be present entirely as sulfonate sulfur and the amounts to about 0.35 *total sulfonate groups* per C_0 unit (coefficient *l*).

The number of *sulfonate methyl esters* per C_9 unit of ALSME-MWL was not determined experimentally since the same procedures, when applied to ALSME-like pure monomers and dimers in our prior work, gave rise to complete acetylation and methyl sulfonate ester formation. However, if all chemically determined sulfur was sulfonate, and if all sulfonate groups in the ALSME-MWL fractions had been converted into methyl ester configurations, then the chemically determined total methoxyl less the presumed total sulfonate ester methoxyl would give the phenolic ether methoxyl groups, e.g., 1.14–0.46 = 0.68/C_9 unit for ALSME-MWL fraction 8.

However, the several phenolic ether methoxyl values estimated in this manner for ALSME fractions are substantially smaller than the phenolic ether methoxyl content of 0.94/C_9 unit found by chemical analysis to be present in the initial MWL (Tables II and III), and also the phenolic methyl ether contents which have been observed at approximately this same level in much prior research conducted in this Laboratory[29,30] and elsewhere. One may speculate that substantial demethoxylation took place in the present experiments during the reactions of sulfonation, acetylation, and/or methyl ester formation, but such a concept we believe to be inapplicable, because earlier studies in this Laboratory and elsewhere[8] have shown that extensive demethoxylation of lignin does not occur during sulfonation under the conditions which were used in the present experiments to carry out the delignification of sulfonation of the initial Western Hemlock wood or the MWL, and moreover, the acetylation and methylation reactions which we used in earlier work[9] to prepare ALSME-like monomers and dimers did not lead to substantial demethoxylation, although the reaction conditions used then were about the same as those now discussed. Thus it appears that substantial phenolic ether demethoxylation did not occur during the several reactions used to prepare ALSME fractions from lignin in wood tissue and that, as a first approximation, we may consider that the initial 0.94 *phenolic methyl ether* groupings present in the unsulfonated MWL continue to present in all ALSME fractions (coefficient *e*).

On this basis, the *sulfonate methyl ester* groupings

Table VI
Average Characteristics of Structural Units of Lignin Sulfonic Acids ($\bar{M} \simeq 4400$; $n \simeq 20$)

	Aromatic segment						Aliphatic segment					
Atom or grouping	C	H	OH	OCH_3	-OX[a]	-CX[a]	C	H	OH	-OX[a]	-CX[a]	SO_3H
Coefficient		*c*	*d*	*e*	*f*	*g*		*h*	*i*	*j*	*k*	*l*
Present work[b]	6	2.50	0.25	0.94	0.75	1.56	3.00	4.60	0.85	0.75	1.20	0.35
Glennie model[c]	6	2.50	0.30	1.00	0.75	1.45	3.00	3.95	0.95	0.90	1.25	0.45

[a] For the present work, "-OX" and "-CX" signify the presence of undetermined configurations which probably involve oxygen and carbon atoms, as for example in ether and carbon–carbon linkages, respectively. [b] Unallocated hydrogen and oxygen atoms (coefficients *a* and *b*) amount to about −0.1 and +0.5, respectively. [c] The Glennie model also contains 0.15 and 0.10 carbonyl and ethylenic double bonds, respectively.

present in the ALSME-MWL were estimated (Table V) by taking the difference between the total chemically determined methoxyl groups and the phenolic ether methoxyl group value of $0.94/C_9$, e.g., for fraction 8, $1.14 - 0.94 = 0.20$.

Free sulfonic acid groupings, then, are represented at maximum by the differences between the total and the methyl ester sulfonates and amount to about 0.2 groups/C_9 or less to the extent that sulfur is present in forms other than sulfonic acids.

The numbers of *unallocated hydrogen and unallocated oxygen atoms*/C_9 (coefficients *a* and *b*) were calculated (Table V). It is found that the hydrogen fluctuates randomly around zero and the oxygen around 0.5 atoms/C_9.

For ALSME-W preparations, calculations of this type could be carried out only in part, since elemental analyses were not made on these fractions. By assuming that the integrated proton signal for each ALSME-W fraction reflects the presence of 14 protons per C_9 structural unit, the proportions present of aliphatic and aromatic hydrogens and hydroxyls were calculated. It was found that the trend of aromatic hydroxyl content approximately followed that observed for the ALSME-MWL samples (see Figure 7). For other parameters the trends were similar but with wider variations which suggested that some ALSME-W fractions were incompletely separated from non-LS materials and thus these results are not reported numerically in this paper.

The numbers of the above-discussed atoms and functional groupings estimated from the ALSME-MWL data to be present per C_9 unit in the several fractions on a LS basis are shown in Table V and are plotted in Figure 7 to indicate trends and to provide the smoothed values shown in Table VI for certain characteristics for the average structural unit of a 20-mer LS polymer which has a molecular weight of about 4400.

Valence and Chain Propagation Considerations. Some indications concerning other functional groups, as well as intra- and inter-mer linkages in LS structural units, can be developed from the smoothed analytical results assuming as a first approximation the existence of structural units which are of the phenyl propane type (Figure 6), although a small proportion of the side chains of such units probably contain less than three carbon atoms, as suggested, for example, in Glennie's LS model[8] shown in Figure 8.

For the aromatic segments of the structural units, extensive literature indicates that some of the oxygen remaining unallocated after carrying out the above-described assignments probably is present in aromatic ether linkages. The frequency of occurrence of these linkages has been estimated by subtracting the sum of the smoothed numbers of aromatic hydroxyl and aromatic methoxyl ether groupings (i.e., 0.25 and 0.94, respectively) from 1.94, the total number of oxygen linkages presumed to be associated with the aromatic nucleus of the structural unit, to yield 0.75/C_9 unit (coefficient *f*).

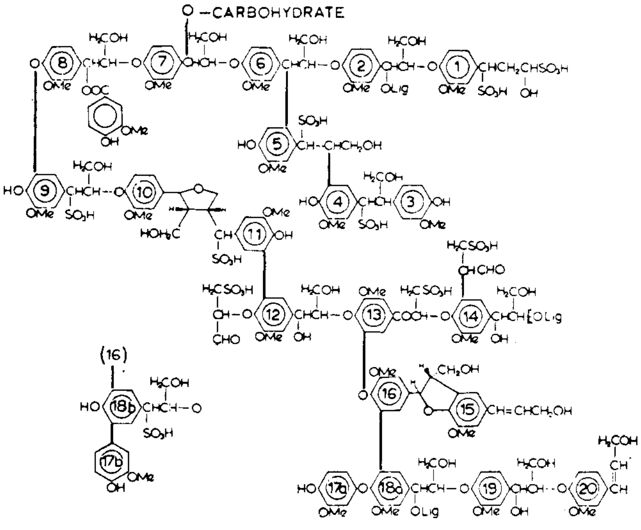

Figure 8. Model structure for lignin sulfonates by Glennie.[8]

The total number of linkages from aromatic carbon atoms to other carbon atoms (coefficient *g*) was estimated by subtracting from six (the total number of aromatic valence bonds available) the sum of the smoothed numbers of experimentally determined aromatic protons (coefficient *c*) and the estimated numbers of aromatic protons hydroxyl, aromatic methoxyl, and aromatic ether groupings (coefficients *d*, *e*, and *f*), i.e.,

$$\text{coefficient } g = 6.00 - [2.50 + 0.25 + 0.94 + 0.75] = 1.56$$

Of these linkages, one C_9 unit (coefficient g_1) is presumed to join the aromatic ring with the α carbon atom of the propyl side chain. In addition, since the basic LS polymer chain may be considered to be propagated by the presence of one oxygen–ether or carbon–carbon linkage between two structural units, and since the aromatic ether linkages appear to amount to only about 0.75/C_9 unit (coefficient *f*), then approximately $1 - 0.75 = 0.25$ aromatic ring linkages/C_9 unit are needed as minimum for chain propagation. These linkages are assumed to connect aromatic ring carbon atoms with carbon atoms of the propyl side chain of adjacent structural unit (coefficient g_2). Coefficient *g* turns out to be larger than the sum of coefficients g_1 and g_2, and the difference is:

$$\text{coefficient } g_3 = 1.56 - [1.00 + 0.25] = 0.31/C_9 \text{ unit}$$

For the side chains of the structural units, the difference between the available eight valence bonds, and the sum of the measured numbers of aliphatic hydrogen and hydroxyl groupings (coefficients *h* and *i*) and the estimated number of aromatic ether and aromatic carbon to side chain linkages derived on the basis of the above-stated considerations (coefficients j, k_1, and k_2), yields the estimated number of unaccounted for bonds for linkages associated with the structural unit side chains, i.e.,

$$\text{coefficient } k_3 = 8.00 - 4.60 + 0.85 + 0.75 + 0.25 + 1.00] = 0.55/C_9 \text{ unit}$$

Coefficients g_3 and k_3 reflect inherent inaccuracies in experiments or assumptions, the presence of linkages which bring about or contribute to intra- or inter-unit crosslinking or chain branching in the LS polymer, and/or the presence of other groupings.

Polymer Characteristics. The phenolic hydroxyl content of the LS fractions decreases and seems to approach a constant value of about 0.25 per C_9 unit (Figure 8) as molecular weight rises to about 4000–5000 or higher (DP $\geq$ 20). Thus, as LS preparations increase in molecular weight to the levels of 10,000 and 100,000 and higher, as observed in this laboratory and elsewhere, the structural units which contain free phenolic hydroxyl, and also those which do not contain free phenolic hydroxyl, seem to be added in a constant proportion of about 1:4. This suggests a significant degree of order in the LS polymer structure.

Glennie, after reviewing the extensive literature on lignin and lignin sulfonates published over the years by Klason, Hagglund, Erdtmann, Freudenberg, Kratzl, Adler, Gierer, and numerous others, recently published[8] the speculative structure for lignin sulfonates shown in Figure 8. For this 20-mer LS model, we have calculated coefficients representing the frequency of occurrence per C_9 unit of certain atoms and functional groupings of present interest but excluding the -O- carbohydrate residues, and the unnumbered ester-linked phenyl entities indicated as attached to structural units 7, 2, 14, 18A, and 8, respectively.

Comparison in Table VI of the now-estimated parameters with the characteristics of the Glennie model shows considerable agreement, although some departures are evident: (a) our aliphatic proton content is considerably higher than that in the Glennie model, perhaps because of the existence of some structural differences between MWL and the LS preparations upon which his model was based; (b) our unallocated oxygen atoms (coefficient b) and also our prospective inter- or intra-structural unit linkages (coefficients g_3 and k_3) are unexpectedly high, probably because of the presence of some carbonyl, carboxyl, and other groupings which were not measured in present work, because the precision of the experimental data is not as high as is desired, and also because some calculations are based upon assumptions which without doubt are less than fully adequate.

We hope that the now reported procedures and results are found to be helpful in evaluating proposed lignin sulfonate structures, and in stimulating future higher precision experimentation, especially with both proton and ^{13}C NMR[31] spectroscopy.

Low Molecular Weight ALSME Compounds. Efforts were also made to isolate low molecular weight ALSME compounds by column chromatography. In order to avoid the disturbing effects of ionic strength upon the chromatographic behavior of LS in aqueous solution in relation to Sephadex gels,[3] certain ALSME-W fractions dissolved in methanol were subjected to chromatography using the Sephadex gel LH 20. The resultant elution patterns (Figure 9) showed that fractions 9–13 contained important amounts of two low molecular weight substances. Fraction 8 exhibited an LH 20 peak which gave NMR signals characteristic of the previously isolated and above-described (Figure 5) vinyl sulfonic acid side chain.[26,27] Fractions 7 and 6, which are of higher average molecular weights, exhibited about ten significant chromatographic concentration peaks.

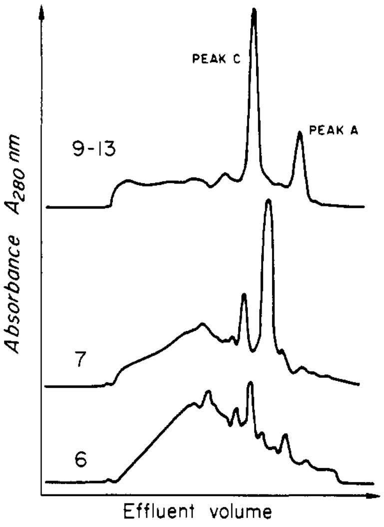

Figure 9. Elution Patterns for Sephadex LH-20-W gel chromatography fractionation of ALSME fractions.

From fractions 9 through 13, a small amount of crystalline substance (mp 202–203°C) was isolated from the peak C material of Figure 9. From the peak A material, a glassy amber material was obtained which did not crystallize but softened at about 80–90°C and melted with decomposition at 150–160°C. Both substances appeared as a single sharp spot on TLC (1:1 benzene–ethyl acetate developer; T_f = 0.65 for compound mp 202–203° and 0.60 for compound mp 150–160°). This work is continuing.

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Preparation and Properties of Polydimethylsiloxane and Its Block Copolymers with Styrene

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ABSTRACT: A series of polydimethylsiloxanes and two-block copolymers with styrene of reasonably narrow molecular weight distribution has been prepared using the monomer hexamethylcyclotrisiloxane. The initiator was *sec*-butyllithium. Evidence was found for a low level of side reactions which results in the molecular weight distributions becoming broader at very high molecular weights. Similarly block copolymers with $M > 2 \times 10^5$ were contaminated with both homopolymers. Purification methods to remove the homopolymers are described. The solution properties of polydimethylsiloxane agreed in general with earlier studies which used fractions produced by polymerization of octamethylcyclotetrasiloxane. The intrinsic viscosities of the block copolymers are, unlike those of styrene–isoprene two-block copolymers, greater than the average of those of the homopolymers. This suggests greater segregation of the two types of segment. The optical properties of the block copolymers are rather unusual. Refractive index increments of the two types of segment are markedly different and in toluene opposite in sign. The overall refractive index increment can therefore be rather small and the P_θ function under these conditions greater than unity at finite angles. Zimm plots of unusual form are then observed. These effects are explained in terms of the Benoit theory of light scattering from block copolymers.

The catalyzed ring opening polymerization of octamethylcyclotetrasiloxane (D_4) to form high polymers is a well-known reaction.[2a] The polymerization is of the equilibrium type and besides linear polymer, cyclic structures of which the monomer (D_4) is a major constituent exist in solution. A recent communication[2b] has stressed the use of hexamethylcyclotrisiloxane (D_3) as monomer. It is claimed that under certain conditions it polymerizes to give linear polymer of negligible cyclosiloxane content at a much more rapid rate. A suitable initiator is butyllithium which can be mixed with D_3 in hydrocarbon solvents to form $Bu{\cdot}Si{\cdot}(CH_3)_2OLi$.[3] No polymerization occurs even in the presence of excess D_3 until a donor solvent such as tetrahydrofuran is added, when a reasonably rapid polymerization starts to give near monodisperse polymers.[2b] Equilibration reactions do occur[4] but these are slow compared with the polymerization rate and so can be minimized by termination of the reaction before complete conversion. Block copolymers can be prepared by the replacement of butyllithium with polystyryllithium.[5-7]

This investigation describes the preparation and characterization in solution of a series of homopolymers and block copolymers of polydimethylsiloxane. Extensive studies of solution properties of styrene–methyl methacrylate and styrene–diene block copolymers can be found in the literature. In some respects the styrene–dimethylsiloxane polymers would be expected to possess interesting properties but a detailed description has not until now been disclosed.

Experimental Section

D_3 obtained from Pierce Chemical, Aldrich Chemical, or supplied by Dr. P. Juliano, General Electric Co., was first zone refined over 40 cycles. The top 75% of the column was then transferred to a flask containing calcium hydride. The flask was evacuated and benzene was distilled in to form a 40% solution which became slightly viscous after standing overnight. Solvent and monomer were distilled off in vacuo. The residue contained some polymer. A solution of polystyryllithium was added via a break-seal to the D_3–benzene mixture. After 1 hr the latter compounds were sublimed off and the solution was subdivided into break-seals. These had previously been washed with butyllithium in benzene followed by rinsing with the solvent. The purification of benzene and tetrahydrofuran (THF) to the standards required for anionic polymerization has been described in earlier publications.[8,9] 1,2-Bis(2-methoxyethoxy)ethane (Triglyme/Eastman) was twice distilled from sodium metal followed by transferral to the vacuum line where it was treated with sodium–potassium alloy before distillation into ampoules. *sec*-Butyllithium prepared in vacuo from *sec*-butyl chloride and lithium metal was purified by a short path distillation in vacuo, diluted, and subdivided into ampoules. The ampoules for initiator and triglyme were cleaned by the same procedure described above for the break-seals.

All polymerizations were carried out in a sealed vacuum apparatus using conventional break-seal techniques. First the *sec*-butyllithium and D_3 were mixed in benzene at 30° and allowed to react for 3 hr. At this point either an equal volume of tetrahydrofuran or enough triglyme to form a 4% (v/v) solution was added. The initial concentration of D_3 was 5–10%. Polymerization at 30° was allowed to proceed to 50–75% conversion until terminated by the addition of a small amount of chlorotrimethylsilane. The lower conversions were used in the preparation of polymers of higher molecular