Engineering Plastics from Lignin. XVI. Starlike Macromers with Propylene Oxide

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Synopsis

Starlike macromers were prepared from hydroxypropyl organosolv lignin by reaction with propylene oxide, and they were analyzed by a combination of conventional analysis techniques. The average number of arms per macromer was controlled by partial capping with an alkoxy group; and the average length of arms by the degree of chain extension with propylene oxide. Analysis methods included treatment with hydriodic acid followed by gas chromatographic separation of alkyl iodides (HI/GC), UV spectroscopy, H-NMR spectroscopy, and thermal analysis. The results were consistent with a hypothetical pentameric model structure having between two and six radiating arms, each with a length of between 1 and 4 propylene oxide units. The UV method was best qualified to determine degree of chain extension, while HI/GC was best suited for analyzing average number of arms per macromer fragment. The synthesis and analysis of starlike macromers from lignin is viewed as an important stepping stone for the formulation of lignin-based engineering plastics and multiphase materials.

INTRODUCTION

Previous research on engineering plastic from lignin has demonstrated that it is possible to attach an extended poly(propylene oxide) (PPO) chain onto lignin, and that average chain length (expressed as "molar substitution") determines molecular weight, T_g, and functionality.[1] Following crosslinking with diisocyanates, polyurethane films from chain extended hydroxypropyl lignin had (a) single glass transition temperatures, and these varied between -53 and 101°C; (b) variable (by 2.5 orders of magnitude) crosslink density (M_c); and (c) Young's moduli ranging between 7 and 1300 MPa. This previous research[1] had demonstrated that material properties of lignin-based thermoset plastics can conveniently be engineered via chain extension with propylene oxide.

Chain extension with propylene oxide proceeds indiscriminately on any and all hydroxy functional groups[2,3] of hydroxypropyl lignins, and there are usually between 1.2 and 1.4 OH groups per average C_9 repeat unit, or 6–9 wt %.[4,5] With number average molecular weights ranging between 1 and 5×10^3 g M^{-1}, this means that there are molecular fragments with an average of between 6 and 30 functional sites available for chain extension with an OH reactive agent. This type of multifunctional macromolecular monomer,

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or "macromer,"[6] gives easy access to segmented copolymers and thermosets. In order to gain greater control over chemical (i.e., aromatic content and functionality) and physical characteristics of the macromer (i.e., T_g, viscosity, etc.),[7] it becomes desirable to limit the number of functional sites available for chain extension (i.e., the creation of "dangling arms") to a target number, preferably between 2 and 4. Starlike macromers are thus produced with length of arms controlled by degree of chain extension and the number of arms controlled by reduction in reactive functionality.

Although the chemistry of an engineered starlike macromer may be relatively simple, its analysis in relation to a given (hypothetical) macromer structure is bound to be complex. This article therefore examines the applicability of conventional analysis techniques for the purpose of quantitatively describing starlike macromers from lignin, having been produced by a combination of chain extension and etherification reaction.

MATERIALS AND METHODS

Materials

Lignin. The lignin employed in this study was an organosolv (ethanol) lignin supplied by the Biological Energy Corporation of Valley Forge, PA. This was isolated from aspen wood chips. Its number average molecular weight ($\overline{M_n}$) was found to be 900 g M^{-1} by vapor pressure osmometry. Its chemistry has been described elsewhere.[4]

Hydroxypropyl Lignin (HPL). The hydroxypropyl lignin derivative was obtained in accordance with earlier reports.[8,9]

Methods

Modification Reactions

Ether Capping. The aliphatic OH groups of HPL were partially capped by reaction with diethyl sulfate ($DESO_4$) in aqueous KOH at room temperature.[5] An about 20% HPL solution in aq acetone was charged with sufficient (solid) KOH to maintain an alkaline medium of pH > 12 throughout the reaction. A variable amount of $DESO_4$ was then added dropwise into the solution, and the reaction was kept going overnight under a constant flow of N_2. The reaction was terminated by adjusting the pH to 2–3.5 with 5*N* HCl, and heating to > 80°C in order to inactivate any remaining $DESO_4$. The reaction product was extracted from the solution with chloroform in a separatory funnel, and, following evaporation, the resulting syrup was precipitated in water, filtered, washed, and freeze-dried.

Chain Extension Reaction. Chain extension with propylene oxide of HPL (CEHPL) and its partially ethylated derivative was accomplished in accordance with a procedure given previously.[1] Reaction with PO in toluene using KOH as catalyst, isolation by sequential liquid–liquid extraction with hexane and acetonitrile as well as by dialysis from aqueous methanol, and recovery from aqueous medium by freeze drying were repeated several times in order to achieve sufficient chain extension.

Analysis Methods

Hydriodic Acid / Gas Chromatography. A modified Zeisel technique,[10] combined with gas chromatographic separation of alkyliodides,[11] was applied for the evaluation of degree of capping by ethoxyl groups, and for the determination of degree of chain extension by propylene oxide. *N*-iodopropane served as internal standard. Microreaction vessels (by Supelco with 5 mL capacity) equipped with Mininert valve tops were charged with HPL or CEHPL, adipic acid, internal standard (i.e., l-iodopropane), and HI. The reaction took place during 1 h at 140°C with frequent shaking. The alkyliodides produced during the reaction were sampled directly from the microreaction vessel and injected into a Varian 3700 gas chromatograph. The oven temperature was 45°C; the injection port and detector temperatures were 210°C, and N_2 was the carrier gas at a pressure of 20 psi. Quantitation was achieved with a CDS 111L data system.

Ultraviolet Spectroscopy. Absorptivity coefficients were determined by dissolving lignin derivatives in methanol to known concentration, and measuring absorbance at 280 nm on a Varian/Cary 219 UV-VIS spectrophotometer.

H-NMR Spectroscopy. H-NMR spectra were obtained from peracetylated lignin derivatives on a Brucker 270 MHz instrument using deuterochloroform as solvent and TMS as internal standard. The results were interpreted in relation to procedures described previously.[1,12]

Thermal Analysis. Glass transition temperatures were determined by dynamic mechanical thermal analysis (DMTA) using a Polymer Laboratories Ltd. instrument. T_g's were determined with dog bones prepared by injection-molding molten blends with thermoplastic polymers having T_g's more than 20°C removed from those of the lignin derivative. The injection molding procedure using polyblends with lignin has been described elsewhere.[13] Dog bones were analyzed over the temperature range of $-100-+100$°C at a heating rate of 4°C/min. Frequency was 10 Hz and strain factor was $\times 4$. Both the dynamic storage modulus and the damping factor were recorded as functions of temperature.

Titration of Total OH Content. The total hydroxy content of lignin derivatives was determined by acetylation and back titration[14] of free acetic acid using a Brinkmann E576 Potentiograph. Vanillyl alcohol served as standard for calibration purposes.

RESULTS AND DISCUSSION

Chemistry

The chemistry of lignin modification by alkoxylation primarily involves reactions of OH groups, and at least initially of phenolic hydroxyls.[8,9] The chemistry of hydroxypropyl lignin necessarily involves reactions of aliphatic OH groups.

The approximate structure of a hydroxypropyl organosolv lignin is shown in Figure 1. This structural scheme is based on available analytical information, with which it produces good agreement.[4,5,15] Its molecular configuration reflects pentameric structure, or a molecular weight of ca. 1000 (before modification). Molar substitution, functionality, and degradation and spectro-

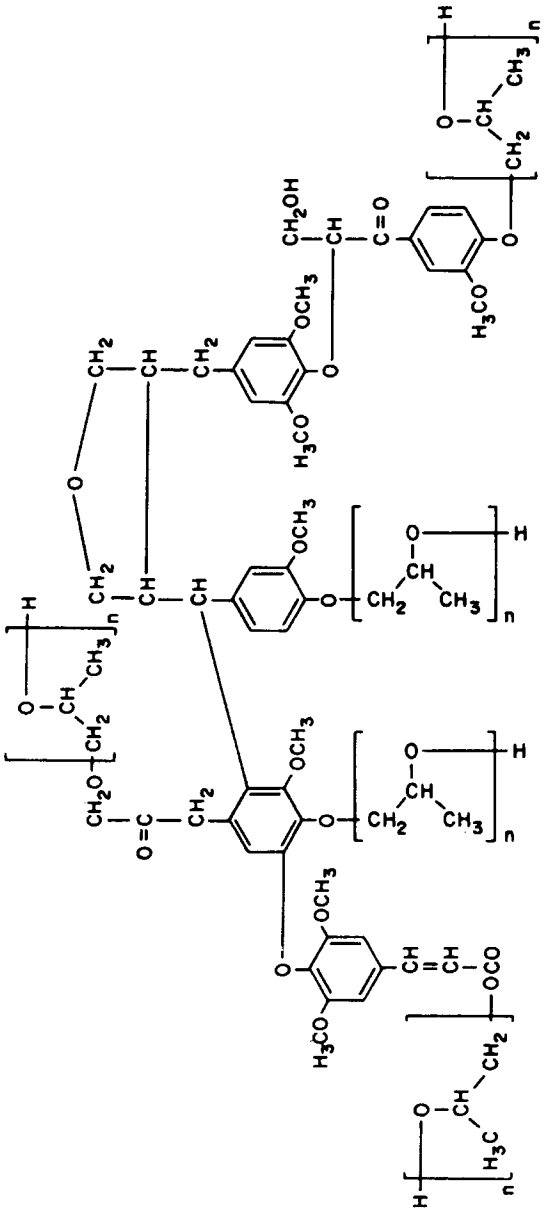

Fig. 1. Schematic representation of a hydroxypropyl (organosolv) lignin derivative ($n = 1$).

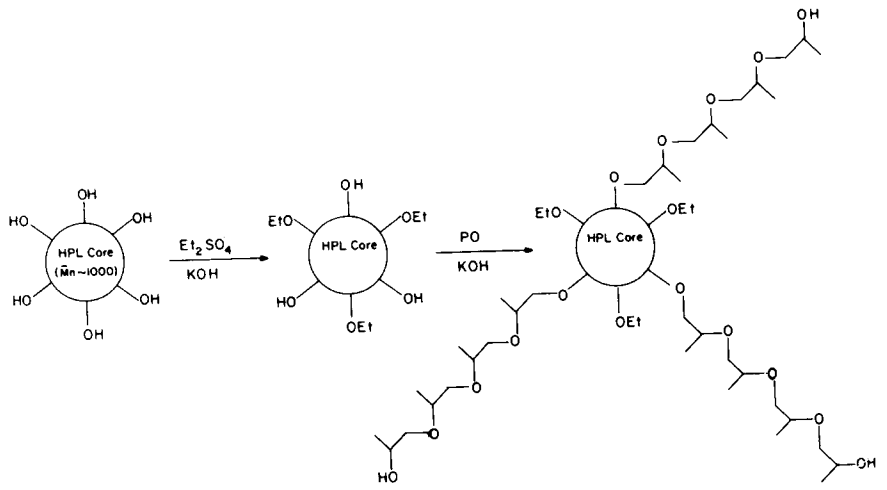

Fig. 2. Schematic representation of the synthesis route for a trifunctional macromer.

scopic behavior all reflect experimental results given earlier.[4,5,15] This structure is not meant to represent a unique chemical configuration since many alternatives could be advanced with equal justification; however, this is a suitable schematic representation of an average hydroxypropyl organosolv lignin molecule.

The structure of Figure 1 is expected to produce a macromer with six protruding propylether arms unless its OH functionality is reduced from the original value of 6. This reduction is accomplished with $DESO_4$ for convenience and practicality, but many alternatives are available. Butyl monoisocyanate has been employed previously for reducing OH functionality of HPL in a related study.[16] Hydroxy capping to the extent of 50% can be expected to produce a trifunctional starlike macromer on the average, with propyl ether chains serving as functional arms. This is illustrated schematically in Figure 2. A starlike macromer with reduced functionality must be considered as inherently superior to an alternate configuration with an unrestricted number of extremities, since this allows the construction of block type networks with greater balance between the contrasting components, (high modulus) aromatic center and (low modulus) aliphatic ether chain. It is this balance that must be engineered carefully for control of material properties. Other arm chemistry is possible, but the analytical rules established here should have general applicability.

Analysis

HI / GC Method. Treatment of HPL with hydriodic acid produces a mixture of methyl and isopropyl iodide, which can be separated by gas chromatography.[11] Using ethylation for capping adds ethyl iodide to the mixture of reaction products.[5] Normalization of ethyl and isopropyl iodide to methyl iodide allows the determination of macromer architecture in terms of functionality (i.e., number of arms) and molar substitution (i.e., length of arms). Analytical results obtained with partially blocked organosolv HPL

TABLE I
Analytical Macromer Characteristics in Relation to Functionality (i.e., Number of Arms)

	Experiment	Model (Fig. 1)
I. HPL (starting material)		
M_n (g M^{-1})	1200	1286
OCH_3 (wt %)	15.7	16.83
OH (wt %)	8.33	7.93
OH groups/macromer	5.9	6.0

II. Capped HPL	Number of OH groups macromer											
	5.2	4.8	4.3	4.0	3.6	2.1	5	4	3	2	1	0
OH (wt %)[a]	7.45	6.85	6.07	5.73	5.05	3.03	6.47	5.07	3.72	2.43	1.19	0
EtI/MeI (molar ratio)	0.18	0.28	0.42	0.53	0.70	1.07	0.16	0.31	0.47	0.63	0.78	0.94
Ethoxy (wt %)[b]	3.06	4.63	6.70	7.59[c]	9.40	14.77[c]	3.42	6.71	9.85	12.88	15.78	18.57
Degree of capping (%)	11	18	27	31	39	64	17	33	50	67	83	100

[a] Data given are those obtained from the expected relationship between ethoxy and hydroxy contents; actual hydroxy contents were extremely variable and unreliable, esp. at low OH contents.

[b] Parent organosolv lignins had a native ethoxy content of 0.73%, which was deducted.

[c] Determined on the basis of the EtI/MeI ratio by HI/GC analysis; and this ratio's relationship to ethoxy content.

TABLE II
HI/GC Analytical Macromer Characteristics in Relation to Average Degree of Chain Extension (i.e., Average Arm Length)

Macromer functionality	Level of chain extension[a]	*i*-PrI/MeI molar ratio	No. avg. PO units per arm (normalized)
5.9	A	0.89	1.0
	B	2.21	2.5
	C	3.43	3.9
5.2	A	0.87	1.0
	B	2.14	2.5
	C	3.46	4.0
4.3	A	0.55	1.0
	B	1.66	3.0
	C	2.16	3.9
4.0	A	0.76	1.0
	B	1.93	2.5
	C	2.48	3.3
3.6	A	0.55	1.0
	B	1.46	2.7
	C	2.21	4.0
2.1	A	0.75	1.0
	B	1.21	1.6
	C	1.25	1.7

[a] Level of chain extension was 0.0 (A), 1.5 (B), and 3.0 g PO/g HPL (C).

macromers, and those expected for the molecular model shown in Figure 1, are given in Table I. For a starting macromer with an average number of functional (OH) groups of six, hydroxy content declines, and ethoxy content as well as ethyl to methyl iodide (molar) ratio increase as the degree of capping with $DESO_4$ increases. Thus, knowledge of molecular weight, hydroxy content (per macromer), and degree of capping permits the determination of macromer functionality in terms of average number of arms.

Since the HI/GC method produces isopropyl iodide from ether linked propoxy units, this method is also qualified to analyze macromer architecture in terms of average arm length. This is illustrated by the data in Table II. The normalized isopropyl iodide content nearly quadruples (i.e., from 0.87 to 3.46) as the number of propyl ether units per arm rises from 1 to 4. This relationship is obviously more significant for macromers with high functionality than for those with high degree of capping.

UV Spectrophotometric Method. The characteristic absorption behavior of lignin at 280 nm wavelength[17] can be used for a quantitative assay of lignin content in a starlike macromer. Studies with ligninlike model compounds demonstrated that UV-absorptivity coefficients decrease in relation to propoxylation, or, in general, to the incorporation of non-UV-absorbing mass.[18] This relationship (Fig. 3) can be employed for determining the extent of propoxylation and chain extension. Since lignin macromers with propylene oxide are typically well soluble in a large number of solvents,[12] the determination of UV absorptivity coefficients at 280 nm provides a convenient method

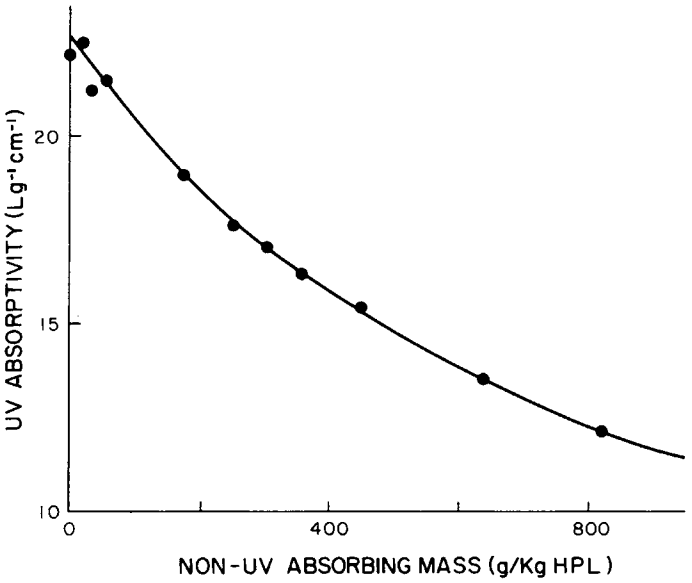

Fig. 3. UV-absorptivity coefficient (280 nm) vs. non-UV absorbing mass in CEHPL.

for determining degree of chain extension (and thus average arm length) at known macromer functionality. Equations relating UV-absorptivity and non-UV-absorbing mass added either by capping or chain extension are derived in relation to experimental data in Table III. Figures for average arm lengths are derived by normalization to the degree of substitution of unextended derivatives.

H-NMR Spectroscopic Method. The H-NMR spectrum of macromers of lignin with PO exhibit significant signals at ca. 1 and 2 ppm (δ values) following acetylation. These represent methyl signals for propoxy and acetoxy groups, respectively. A rise in PO arm length thus gives rise to an increase in signal intensity in the H-NMR spectrum. This information can be employed for calculating average arm length (Table IV). This calculation is, however, complicated by the presence of overlapping ethoxy signals.

Glass Transition Temperatures (T_g). Previous research has demonstrated that chain extension of HPL with PO results in single phase, uniform copolymers exhibiting single glass transitions.[1] It has furthermore been demonstrated that these T_g's vary in relation to chemical composition in accordance with the Gordon–Taylor equation.[19] Thus, an increase in PO arm length can be expected to result in a reduction in overall T_g. Glass transitions were determined using injection molded polyblends with phase-separated thermoplastics in accordance with related studies.[13] Thermal analysis results with starlike macromers of lignin with PO are given in Table V.

Although several samples did indeed show the expected behavior of decline in T_g with chain extension (i.e., the samples with 5.9, 4.3, and 3.6 average macromer functionality), other samples exhibited an unexpected *rise* in T_g with chain extension. This cannot be explained and must be attributed to partial phase mixing of the two blend components in relation to changes in chemistry. Results with these samples were therefore ignored. Other problems

TABLE III
UV-Absorptivity Macromer Characteristics in Relation to Non-UV-Absorbing Mass and Average Degree of Chain Extension.

Macromer functionality	Degree of capping (%)	Level of chain extension	Non-UV absorbing mass from C[a] (g/kg HPL)	Non-UV absorbing mass from W[b] (g/kg HPL)	Non-UV absorbing mass from Total (C + W) (g/kg HPL)	UV-absorptivity a_{280} (L g^{-1} cm^{-1})	PO units per arm Average[c]	PO units per arm Normalized
5.9	0	A	0	0	0	22.1	0.64	1.0
	0	B	0	444.4	444.4	15.3	2.25	3.5
	0	C	0	826.4	826.4	12.1	5.29	8.3
5.2	11	A	15.4	0	15.4	22.4	0.65	1.0
	11	B	15.4	284.6	300.0	17.0	1.50	2.3
	11	C	15.4	621.6	637.0	13.5	4.07	6.3
4.3	27	A	36.9	0	36.9	21.4	0.67	1.0
	27	B	36.9	218.8	255.7	17.6	1.38	2.1
	27	C	36.9	388.9	425.8	15.5	2.79	4.2
3.6	39	A	52.5	0	52.5	21.0	0.68	1.0
	39	B	52.5	116.8	169.3	18.9	0.83	1.2
	39	C	52.5	303.3	355.8	16.3	2.51	3.7

[a]Mass added by capping with an ethyl ether group (i.e., OC_2H_5) is calculated from the following equation: mass added C (g/kg HPL) = $(D)*(F)*(290)*[\overline{M}_n + (D)*(F)*0.29]^{-1}$, where D is the degree of capping with OC_2H_5 in percent, F is the number of OH equivalents of the parent HPL per $\overline{M}_n$, and $\overline{M}_n$ is the number average molecular weight of HPL.

[b]Mass added after chain extension with PO (i.e., OC_3H_7) is calculated from the following equation: mass added, W (g/kg HPL) = $(22{,}100)*(a_{280})^{-1} - 1000 - C$ where 22,100 represents the absorptivity coefficient of (parent) HPL × 1000 and a_{280} is the absorptivity coefficient of the HPL derivative (at 280 nm).

[c]PO units per arm are calculated by the following equations: PO units (avg. number per arm) = $(W)\ (221)*(\mathrm{MS})*[(S)*(a_{280})*(100 - D)]^{-1}$, where S is the propoxy content of the parent HPL in percent and MS is the average molar substitution determined from MS = $(S)\ [\overline{M}_n + (D)*(F)*(0.29)]*(F)^{-1}*(5800)^{-1}$. (Propoxy content in the parent HPL used here was 18.25%.)

TABLE IV
H-NMR Spectroscopic Macromer Characteristics in Relation to Average Degree of Chain Extension (i.e., Average Arm Length)

Macromer functionality	Level of chain extension	Degree of capping	Percent of total H in range[a]			Range 8′/7 (ratio)	PO units per arm (normalized)
			7 (2.5–1.58 ppm)	8 (1.58–0.9 ppm) uncorrected	8′ corrected[b]		
5.9	A	0	22.2	20.5	20.5	0.92	1.0
	B	0	16.4	33.6	33.6	2.05	2.2
	C	0	12.2	44.2	44.2	3.62	3.9
5.2	A	11	21.9	24.0	20.8	0.95	1.0
	B	11	13.9	35.4	32.2	2.32	2.7
	C	11	10.2	34.3	31.1	3.05	3.6
4.3	A	27	17.5	28.3	21.2	1.21	1.0
	B	27	13.0	35.0	27.9	2.15	2.4
	C	27	7.7	35.7	27.9	3.71	4.2
4.0	A	31	9.7	55.3	28.6		
	B	31	11.5	32.8			
	C	31	8.1	38.9			
3.6	A	39	11.9	29.6	19.6	1.65	1.0
	B	39	9.3	34.6	24.6	2.65	2.6
	C	39	10.1	37.7	27.7	2.74	2.7
2.1	A	64	9.4	58.8			
	B	64	7.8	43.5			
	C	64	7.0	45.5			

[a] For assignment of ranges, see ref. 12.

[b] Represents a numerical deduction of signals due to ethoxy–CH_3 signals.[18]

[c] In the calculation of PO units/arm the degree of capping of each HPL was taken in account, as given by the following equation: PO units (number per arm) = $(H^{CE}_{R.8'/7})[(H^{0}_{R.8'/7})*(1 - D/100)]^{-1}$, where $H^{CE}_{R.8'/7}$ is the ratio between the total hydrogen signal in range 8′ to range 7 of each CEHPL (levels B and C), $H^{0}_{R.8'/7}$ is the ratio between the total hydrogen signal in range 8′ to range 7 of each HPL or capped HPL (level A), and D is the degree of capping in percent.

TABLE V
T_g Macromer Characteristics in Relation to Average Degree of Chain Extension (i.e., Average Arm Length)

Macromer functionality	Level of chain extension	T_g[a] (°C)	T_g Change[b] (°C)	Weight fraction PPO (%)	Number of PO units per arm[e]	
					Average	Normalized
5.9	A	71		18[c]	0.63	1.0
	B	50	21	27[d]	1.1	1.8
	C	23	48	52[d]	3.1	5.0
5.2	A	37		19[c]	—	—
	B	55	−23	—	—	—
	C	36	1	—	—	—
4.3	A	68		11[c]	0.65	1.0
	B	49	19	25[d]	1.45	2.2
	C	38	30	37[d]	2.55	3.9
4.0	A	27		—	—	—
	B	50	−23	—	—	—
	C	37	−10	—	—	—
3.6	A	57		10[c]	0.66	1.0
	B	64	−7	—	—	—
	C	45	12	18[d]	1.17	1.8
2.1	A	32		18[c]	—	—
	B	42	−10	—	—	—
	C	42	−10	—	—	—

[a] T_g was determined by DMTA on dogbone-shaped specimens of HPL (or CEHPL) blended with 60–80% of an incompatible (thermoplastic) polymer.

[b] T_g change expresses the change in T_g between the parent (blocked) HPL and the chain-extended HPL. Negative numbers (i.e., an *increase* in T_g in relation to chain extension) cannot be explained and must be based on differences in polymer–polymer interaction behavior based on chemical factors).

[c] PPO weight fraction calculated from HI/GC results.

[d] PPO weight fraction was calculated from the Gordon–Taylor equation (19), using observed T_g's and a k value of 0.45.

[e] PO units per arm are calculated by the following equation: PO units, n (avg. number per arm) = $W_2\ [\bar{M}_n + (D)*(F)*(0.29) - (f)*(58)*(\mathrm{MS})]*[(f)*(58)*(100 - W_2)]$, where W_2 is the PPO weight fraction, $\bar{M}_n$ is the number average molecular weight of the parent HPL, f is the macromer functionality (number of free hydroxy groups available for chain-extension), and MS is the average molar substitution in level A.

TABLE VI
Macromer Arm Length According to HI/GC, UV, H-NMR, and Thermal Analysis (T_g) Methods

Macromer functionality	Level of chain extension	Average arm length by				
		HI/GC	UV	H-NMR	Avg.[a]	T_g
5.9	A	0.89	0.64	0.92	0.82	0.63
	B	2.21	2.25	2.05	2.17	1.3
	C	3.43	5.29	3.62	4.11	3.8
5.2	A	0.87	0.65	0.95	0.82	—
	B	2.14	1.50	2.32	1.99	—
	C	3.46	4.07	3.05	3.53	—
4.3	A	0.55	0.67	1.21	0.81	0.65
	B	1.66	1.38	2.15	1.73	1.43
	C	2.16	2.80	3.71	2.89	2.52
4.0	A	0.76	—	—	—	—
	B	1.93	—	—	—	—
	C	2.48	—	—	—	—
3.6	A	0.55	0.67	1.65	0.96	0.66
	B	1.46	0.83	2.65	1.65	—
	C	2.21	2.51	2.74	2.49	1.17
2.1	A	0.75	—	—	—	—
	B	1.21	—	—	—	—
	C	1.25	—	—	—	—
r^2		0.94	0.95	0.82		

[a] Using data from HI/GC, UV, and H-NMR, only.
[b] r^2 correlation factors were calculated for individual methods in relation to the average values from three methods.

with the determination of T_g by DMTA of injection molded specimens may also result from the presence of such impurities as solvent, or from nonuniform component distribution in the blend, among others. The complexities associated with T_g determination in general, and that of measuring T_g in polyblends of thermoplastic components in particular, make this type of thermal analysis an unreliable method for the determination of chain extension.

Table VI summarizes the data on macromer arm length determinations from the four analysis methods. Only the thermal analysis results were excluded from the calculation of average figures. In general, good correspondence (i.e., high r^2 values) were noted for the individual methods with the averaged figures (Table VI). The analysis methods based on UV and HI/GC proved to be superior to those based on H-NMR and T_g by producing higher confidence levels (i.e., higher r^2 values).

Interpretation in Relation to Model Structure

The effect of reduced macromer functionality, and thus of a reduced number of arms per $\overline{M}_n$, on the properties of a chain extended hydroxypropyl lignin is best illustrated by comparing experimental data with those expected from a hypothetical model structure. Assuming that Figure 1 gives an adequate representation of a hydroxypropyl organosolv lignin, data expected for

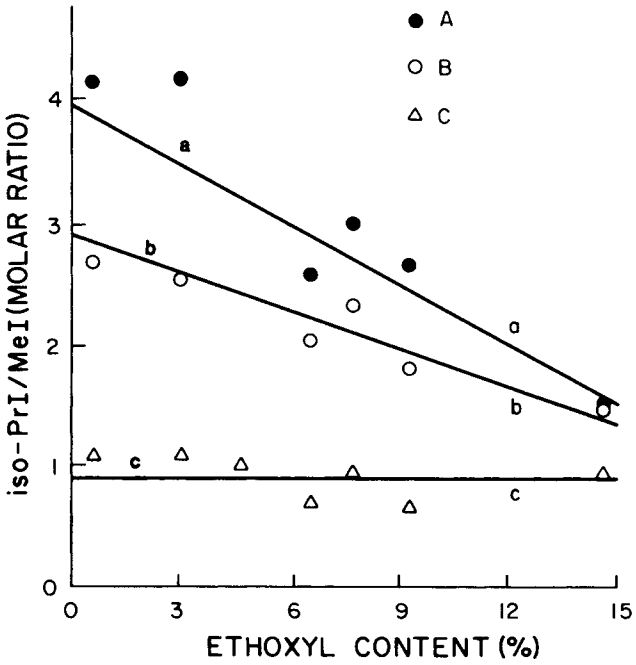

Fig. 4. Relationship between *iso*-PrI/MeI (molar ratio) and ethoxy content of CEHPL with different arm length. [Note: Data points given represent experiments without propoxylation (C) (△) and propoxylated with 1.5 (B) (○) and 3.0 g PO/g HPL (A) (●); and lines represent model values for $n = 4$ (a), $n = 3$ (b), and $n = 1$ (c)].

such a structure following conversion into different types of starlike macromers with propylene oxide should correspond to those obtained experimentally.

Figure 4 illustrates the relationship between the molar ratio of isopropyl iodide to methyl iodide (which represents an adequate method for determining degree of chain extension with PO) and ethoxy content (signifying macromer functionality). It is obvious that experimental data are in good agreement with those of the model for average arm lengths of 1, 3, and 4 propylene oxide units.

Analogous data for the relationship between UV absorptivity coefficient and macromer architecture are given in Figure 5. Again, experimental data agree with those for the model for average degrees of chain extension of 1, 2–3, and 4 PO units per arm.

The relationship between H-NMR signal ratios and degree of capping produces a set of converging lines for the model structure (Fig. 6), and experimental data approach those lines indicating that arms are 1, 2, and 4 PO units long on the average.

Model T_g data reveal poor agreement with experimental data (Fig. 7), as expected.

Figures 4–7 reveal that several techniques exist for analyzing macromer architecture for molecules with high functionality. However, as the number of macromer arms diminishes, analytical differences between starlike macromers with differing arm lengths diminish as well. This is indicated by the fact that all lines (of all figures) converge at ethoxy contents of 15% or above.

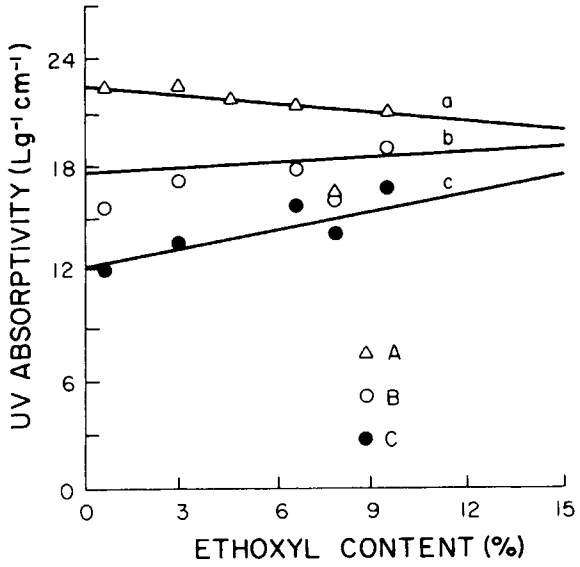

Fig. 5. Relationship between absorptivity coefficient and ethoxy content of CEHPL with different arm length. [Note: Data points given represent experiments without propoxylation (A) (△) and propoxylated with 1.5 (B) (○) and 3.0 g PO/g HPL (C) (●); and lines represent model values for $n = 1$ (a), $n = 2$ (b), and $n = 4$ (c)].

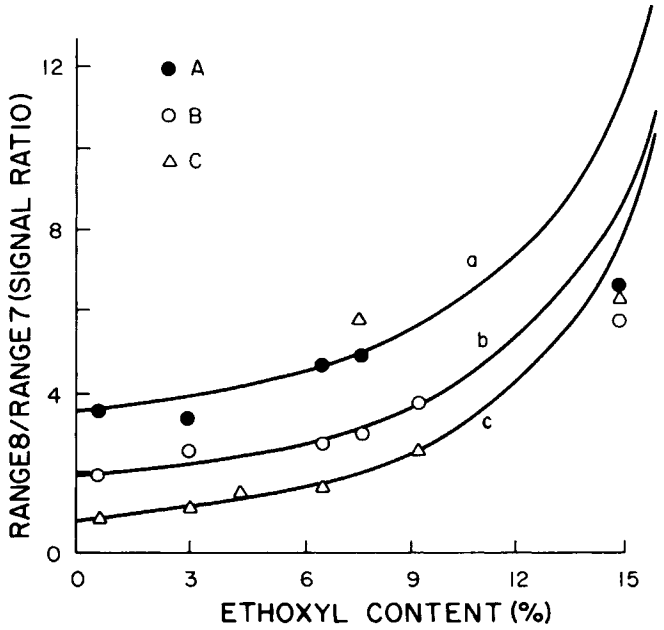

Fig. 6. Relationship between methyl proton signal ratio (ranges 8 and 7) vs. ethoxy content of CEHPL with different arm length. [Note: Data points given represent experiments without propoxylation (C) (△) and propoxylated with 1.5 (B) (○) and 3.0 g PO/g HPL (A) (●); and lines represent model values for $n = 4$ (a), $n = 2$ (b), and $n = 1$ (c)].

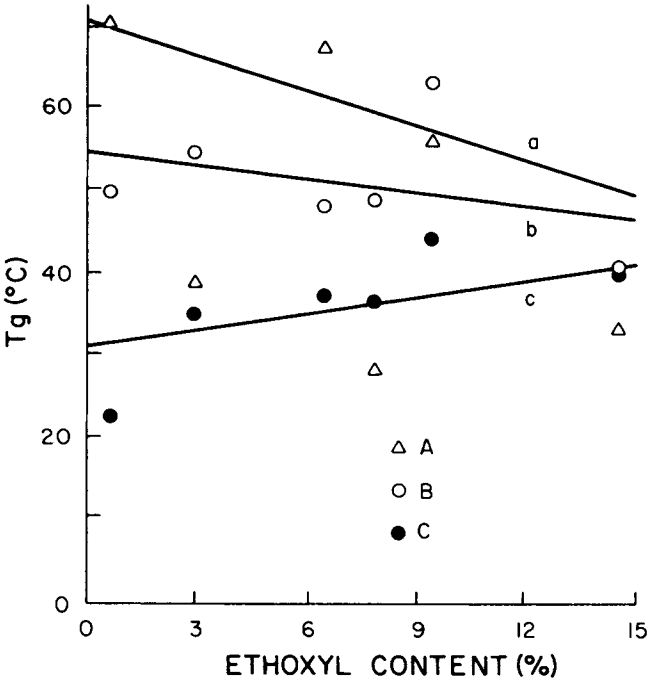

Fig. 7. Relationship between T_g and ethoxy content in CEHPL with different arm length (n). [Note: Data points given represent experiments without propoxylation (A) (△) and propoxylated with 1.5 (B) (○) and 3.0 g PO/g HPL (C) (●); and lines represent model values for $n = 1$ (a), $n = 2$ (b), and $n = 4$ (c)].

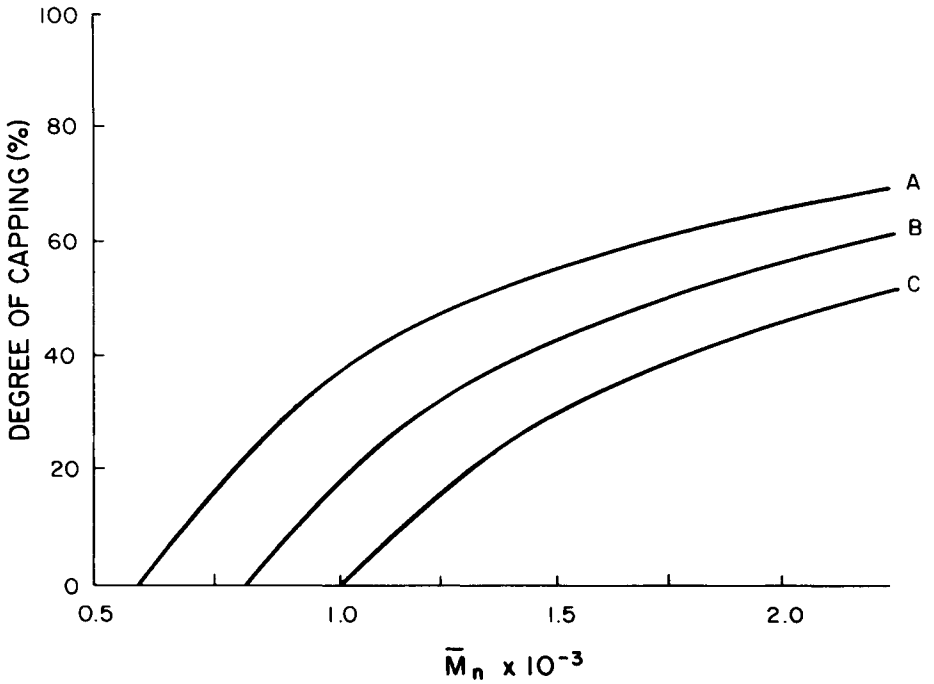

Fig. 8. Theoretical relationship between the required degree of capping and M_n for starlike macromers having (A) three, (B) four, and (C) five functional groups. (Note: For a HPL having 1.3 OH groups/C_9 on the average, and an MS of 1.0).

The design of a target starlike macromer with uniform architecture is limited by the ability to produce precursors with well-controlled functionality. Macromer functionality, in turn, is the consequence of both molecular weight and degree of capping. A larger macromer has higher functionality and requires more capping than a corresponding small macromer molecule for producing a starlike structure with a fixed number of arms. The theoretical relationship between the necessary degree of capping and $\overline{M}_n$ for the synthesis of tri-, tetra-, and penta-functional starlike macromers is illustrated in Figure 8. This relationship was derived for a macromer structure with the features depicted in Figure 1. Results show that the required degree of capping rises with $\overline{M}_n$. The synthesis of a trifunctional starlike macromer from a parent macromer with an $\overline{M}_n$ of 1300 g M^{-1} requires capping of half of the available functional groups. The same molecule would produce a pentafunctional star if only one sixth of all available functional groups were capped. Thus, the engineering of uniform starlike macromers requires the availability of macromer fractions with (a) known average functionality; (b) known molecular weight; and (c) narrow molecular weight distribution.

CONCLUSIONS

The architecture of engineering starlike macromers from lignin synthesized with propylene oxide following partial capping of OH functional groups with aliphatic ethers can be adequately described using HI/GC, UV, and H-NMR spectroscopy. Thermal analysis is less reliable for determining chemical composition. Quantitative information regarding molecular weight ($\overline{M}_n$) and functionality, and a readily detectable blocking agent, are necessary for establishing average macromer composition. Conventional HI/GC, UV, and H-NMR spectroscopy are suitable methods for determining average arm lengths of starlike macromers from lignin and propylene oxide.

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