Reactions of Quinomethides: Stereoselective Oligomer Syntheses by Michael Additions

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ABSTRACT: Novel lignin-model polymers have been prepared from a β-aryl ether quinonemethide by base-catalyzed condensations which were either chemically or electrochemically initiated. The principal intermonomer linkage appears to be of the C_α–O_4 ether type. The key bonding features and functionalities are similar to those exhibited by lignins, except the latter has a much higher level of C_β–O_4 intermonomer linkages. The polymers can be prepared with weight-average molecular weights of 700–7000 and small polydispersities (1.2–1.5). These simple polymers could be highly suitable as standards for the calibration of molecular weight distributions of lignins in the low molecular weight range. The stereochemistry around the α- and β-side-chain carbons of the polymers was shown to be dependent on the nature of the countercation present during polymer preparation. In the presence of tetraalkylammonium cations, the thermodynamically more stable erythro isomer is preferentially formed. The threo isomer is preferentially formed in the presence of alkali metal cations. An explanation based on the application of Cram's empirical rule concerning nucleophilic addition reactions, combined with the well-established template roles of alkali metal cations, is proposed.

Introduction

Cleavage of β-aryl ethers is an important reaction in the depolymerization of lignins[1] and the making of paper from wood. The key intermediates in the depolymerization reaction in alkaline solutions are lignin quinonemethides.[2] In alkaline solution containing HS^- and/or AHQ^{2-} ions, these intermediates can undergo fragmentation at the β-aryl ether bond, which leads to wood delignification. The quinonemethides (QMs) of lignin can also be converted into relatively stable vinyl ethers or undergo condensation reactions with phenolate ions resulting in the formation of stable C–C bonds; both processes contribute to the formation of residual lignins.[3] Anthraquinone is a well-known catalyst for the depolymerization reaction.[4] The mechanism of catalysis of such a cleavage is a topic of considerable interest. Rival hypotheses include the postulation of quinonemethide/anthraquinone adducts as key intermediates[3,5,6] as opposed to a catalytic mechanism involving single electron transfer between anthraquinone radical anions and quinonemethides.[7,8]

In nonaqueous and mixed solvents, evidence was added to the electron-transfer mechanism by using electrochemical techniques such as cyclic voltammetry[9] and low concentrations of quinonemethides in the presence and absence of anthraquinone. In order to understand the competing reactions in more detail, so that reaction products and intermediates could be measured and isolated, it was necessary to work at higher concentrations of quinonemethides. The application of high-performance size exclusion chromatography[10] to the analysis of key reaction products and intermediates has led to a better understanding of the reaction mechanism and also to the discovery of a convenient method for the preparation of the well-defined lignin model polymers, reported here.

These lignin model polymers are very important because of their close similarity to lignins in terms of key functional groups and bonding. Determination of the absolute molecular weights of these polymers is ongoing and will allow their use as calibration standards for the measurement of important lignin polymer properties such as molecular weight distributions by high-performance size exclusion chromatography. Earlier work has shown that polystyrenes, commonly employed standards, cannot be used in high fractional polarity solvents, which are usually the most useful solvents for lignins.[11] The discovery of reproducible model polymers will lead to a better understanding of solute–gel interactions and to reliable calibration procedures.

Experimental Section

Quinonemethide Preparation. The method of Ralph and Young[12] was employed in the preparation of the quinonemethide (QM).

Chemical Polymer Preparation. A solution of 10 mL of QM (approximately 50 mg) in dichloromethane was evaporated almost to dryness under a stream of nitrogen. The QM was then dissolved in 5–45 mL of acetonitrile (AN) or dimethylformamide (DMF) (UV grade, Burdick & Jackson, used without further purification). To the quinonemethide solution was added about 0.07 mL of either tetra-*n*-butylammonium hydroxide (TBAH, 0.062 M) or sodium hydroxide (0.066 M) or lithium hydroxide (0.064 M). The solution was neutralized with 0.04 M HCl. The solvent was evaporated by vacuum distillation. The residue was then dissolved in dichloromethane (10 mL) and extracted with water (3 × 10 mL) to remove any salts that were present. Typical yields of polymers prepared in acetonitrile were 40 mg (80%) from TBAH and NaOH. Elemental Anal. Calcd: C, 70.44%; H, 6.35%; O, 23.20%. Found: C, 72.24%; H, 6.54%; O, 21.22% (from TBAH); C, 69.46%; H, 6.35%; O, 24.19% (from NaOH) (Huffman Laboratories, Golden, CO).

Electrochemical (EC) Polymer Preparation. The cell employed and equipment are described in ref 9. Fifteen milliliters of catholyte solution (dimethylformamide, UV grade, Burdick & Jackson) containing 0.1 M tetra-*n*-butylammonium (TBA) or tetraethylammonium perchlorate (TEAP) was employed to dissolve the QM (approximately 50 mg), prepared as described above. Electrolyses were carried out potentiostatically at −0.85 V vs. Ag/AgCl. About 0.02 faraday/mol of the quinonemethide caused complete conversion of the QM into the polymer. The solvent was evaporated by vacuum distillation. Using TEAP, the polymer could be obtained free of salt contamination by dissolution in dichloromethane (10 mL), followed by washing with water (5 × 10 mL). After drying with anhydrous sodium sulfate and filtering, the dichloromethane was removed on a rotary evaporator. TBAP could only be removed from the polymer by using a silica gel column. Typical yields of the polymer prepared with TEAP were 34 mg (68%) after purification.

HPSEC. The Hewlett-Packard 1090 liquid chromatograph was employed with the HP 1040 diode array detector supplied with an eight-channel integrator. Hewlett-Packard's HP1090 GPC

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Table I
Characteristic Polymer Average Molecular Weights from HPSEC and Estimated Average Molecular Weights by NMR

	HPSEC apparent					NMR av	
type	M_p	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	PI[b]	$R \pm 1$[a]	molec. wt
EC/TBAP	2110	1540	2270	3020	1.5	9	2670
EC/TBAP	2850	2420	3160	4100	1.3	11	3300
EC/TEAP	1365	930	1340	1760	1.4	3.5	1040
NaOH	5800	3925	7350	10170	1.9	18	5350
TBAH	3470	2600[c]	3710	4680	1.4	12	3560
TBAH	4730	2870	4650	6550	1.6	9	2670[d]
TBAH	3470	2750	4220	6050	1.5	10	2970[d]
$NaOCH_3$	4730	3715	5069	6330	1.4	20	6000
LiOH	1185	1040	1210	1370	1.2	4	1250

[a] R = ratio of α-proton/phenolic protons. [b] PI = polydispersity ($\bar{M}_w/\bar{M}_n$). [c] Vapor pressure osmometry, $\bar{M}_n$ = 2550. [d] NMR samples contaminated with small amount (1%–2%) of monomers; actual molecular weight could be 300–600 higher.

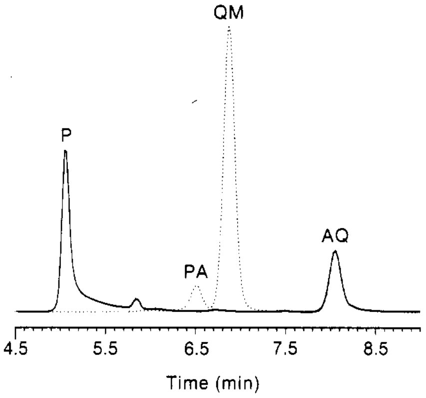


Figure 1. Chromatogram (50 Å, 5-μm PL-gel column) of catholyte solution before (···) and after electrolysis (—) of quinonemethide (QM) in the presence of anthraquinone (AQ) at −0.85 V vs Ag/AgCl (P = polymer, PA = precursor alcohol).

system was used to calculate the polymer average molecular weights from the HPSEC. Fifty-angstrom (5 μm, 300 × 7 mm) and 1000-Å (10 μm, 300 × 7 mm) Polymer Laboratories PL-gel (polystyrene–divinylbenzene copolymer gel) columns were used. Calibration procedures and standards are described in ref 11. The mobile phase was tetrahydrofuran (Burdick & Jackson) at 1.0 mL/min flow rate and 26 °C. Injection volumes of 5 μL were employed, either of the solutions used to prepare the polymers (250 μL diluted with 500 μL of solvent) or of solutions made to analyze the polymers after isolation (1 mg/mL range).

NMR. A JEOL FX-90Q spectrometer and the solvents $CDCl_3$ and D_2O (Aldrich) were employed.

IR. A Nicolet 5SXC FTIR was employed with KBr pellets. Main absorption peaks (in cm^{-1}) were at 1637, 1630, 1619, 1593; 1502, 1456, 1256, 1224, 1133, 1125, 1029, and 746.

Vapor Pressure Osmometry. This was determined by Huffman Laboratories, Golden, CO.

Results

The chromatogram of the quinonemethide (QM) and of its precursor alcohol (PA) are shown as the dotted line of Figure 1. After passage of 0.02 faraday/mol, the corresponding chromatogram is illustrated in the full line of Figure 1. Most electrochemically prepared polymers in DMF exhibited apparent weight-average molecular weights ($\bar{M}_w$) in the 2000–3000 range, independent of the starting QM concentration over the 10–20 mM range (Figure 2). The molecular weights of the chemically prepared polymers in acetonitrile, on the other hand, were directly proportional to the starting QM concentration over the 3–30 mM range. Polymers have been prepared in the 700–7000 weight-average molecular weight range. The UV absorption spectra of the polymer, the starting QM, the precursor alcohol PA, and anthraquinone are compared in Figure 3. The similarity of the spectra of the polymers with that of the precursor alcohol suggests that the polymer contains α-oxygenated functions. Table I presents the peak- (M_p), number- ($\bar{M}_n$), weight- ($\bar{M}_w$), and z-average molecular weights ($\bar{M}_z$) as well as the polydispersities (PI) of the polymers and the corresponding preparation method. Except for NaOH-generated polymers, small polydispersities were observed. There is good agreement between the number-average molecular weight obtained by HPSEC calibrated with polystyrenes and Igepals and the preliminary vapor pressure osmometry measurements on a small amount of sample.

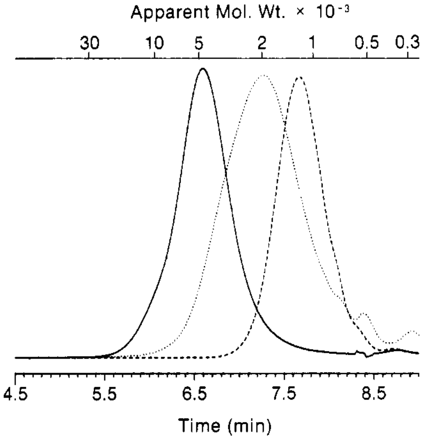


Figure 2. Examples of high-performance size exclusion chromatograms (1000 Å, 10-μm PL-gel column) of polymers prepared from quinonemethide (QM) in acetonitrile electrochemically.

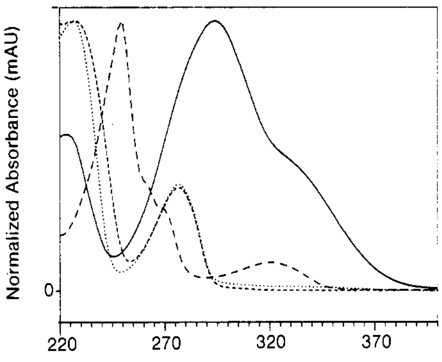


Figure 3. Comparison of UV absorption spectra of starting materials and products from electrolysis of quinonemethide (QM) in the presence of anthraquinone at −0.85 V vs Ag/AgCl (QM (—), PA (···), P (- - -), AQ (– –)). See Figure 1 for abbreviations.

Polymer formation can easily be explained in terms of Michael additions[13] of nucleophiles to the α-carbons of the QM, forming new nucleophiles, the phenolate anions, which continue to propagate the polymerization by attacking another QM until the concentration of QM is es-

Table II
^{1}H NMR Chemical Shifts and Assignments for Tetrabutylammonium Hydroxide and Electrochemically Generated Polymers in Deuteriochloroform

δ, ppm	assignment	δ, ppm	assignment
1.00–1.18	γ-H (threo)	4.36–4.66	β-H
1.28–1.52	γ-H (erythro)	5.00–5.20	α-H
~1.55–1.77	α-OH and H_2O	5.62	phenolic OH
3.46–3.90	OCH_3	6.52–7.00	aromatic H

sentially exhausted or the negative charges are neutralized by protonation or association with cations in general.

An example of an initiation reaction is

$$QM + HO^- \rightarrow MO^- \quad (1)$$

Examples of propagation reactions are

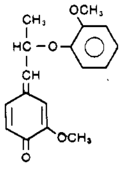
$$MO^- + QM \rightleftharpoons MO\text{–}QM^- \quad (2)$$

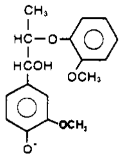
$$MO\text{–}QM^- + QM \rightleftharpoons MO\text{–}QM\text{–}QM^- \quad (3)$$

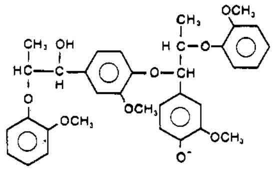
An example of a termination reaction is

$$MO\text{–}(QM)_x\text{–}QM^- + H^+ \rightarrow MO\text{–}(QM)_x\text{–}QMH \quad (4)$$

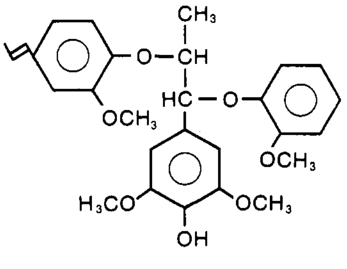
where


QM


MO^-


$MO\text{-}QM^-$

Spectroscopic Characterization of the Polymers. The isolated and purified polymers prepared were subjected to NMR characterization. The ^{1}H NMR spectra of the TBAH and the electrochemically (EC) generated polymers are essentially identical. The main signals and their assignments are assembled in Table II. The spectrum (Figure 4a) is relatively simple with sharp signals compared to those for lignins themselves. The broad doublets centered at 1.12 and 1.42 ppm were assigned to the γ-protons of the threo and erythro configurations, respectively. These assignments are based on those of the syringyl model compound (MD) prepared in erythro and threo configurations by Zanarotti.[14] The ratio of isomers erythro/threo was calculated based on the ratio of the areas of the two doublets, centered at about 1.42 and 1.12 ppm, and was about 4:1 for MD. The ratio (4:1) found for the polymers prepared with TBAH and EC was the same as that found by Zanarotti.


MD (erythro)

The signals of the methoxy protons in these polymers appeared at 3.46–3.90 ppm, values that are similar to those usually found in lignins.[1] The broad multiplet between 4.36 and 4.66 ppm was due to the β-H, and the broad doublet centered at 5.08 ppm ($J_{\alpha,\beta}$ ~ 4.3 Hz) with a shoulder at 5.19 ppm was assigned to the α-H. The small broad singlet at 5.62 ppm, found to exchange readily with D_2O, was assigned to phenolic hydroxy protons. Changing the base from tetrabutyl- to tetraethylammonium hydroxide produced similar polymers. The ratio of erythro/threo isomers is 2:1 in the TEAH case.

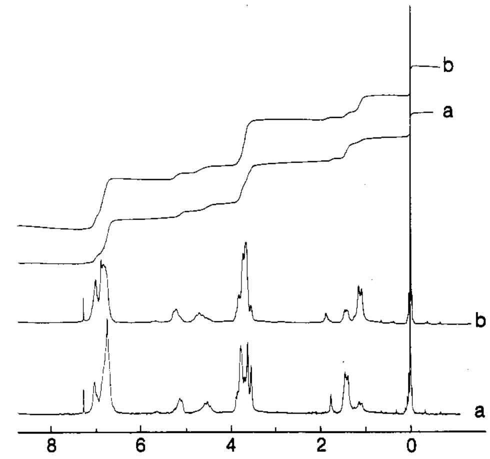


Figure 4. ^{1}H NMR spectra of polymers prepared from quinonemethide (QM) in acetonitrile. Polymer dissolved in $CDCl_3$: (a) 10.6 mM QM solution and addition of aqueous tetrabutylammonium hydroxide; (b) 33 mM QM solution and addition of aqueous sodium hydroxide.

Table III
^{1}H NMR Chemical Shifts and Erythro/Threo Ratios of Lignin Model Polymers Produced in the Presence of Various Cations

cation	proton α	proton β	erythro/threo
Bu_4N^+ electrochemical	5.12	4.51	4:1
Bu_4N^+ chemical	5.12	4.51	4:1
Et_4N^+ electrochemical	5.12	4.52	2:1
Na^+ chemical	5.19	4.68	1:3
Na^+ chemical (methoxide)	5.20	4.69	1:3.7
Li^+ chemical	5.26	4.71	1:10

On changing the base from tetraalkylammonium hydroxide to sodium hydroxide, a significant change in the polymeric product was observed (see Figure 4b). The ratio of isomers erythro/threo, which had previously been found to be 4:1 for both TBAH and EC and 2:1 for TEAH, was essentially reversed to 1:3 for the polymer prepared in NaOH, 1:3.7 for the polymer prepared with $NaOCH_3$, and 1:10 for the polymer prepared with LiOH. In addition, the multiplet centered at 4.51 ppm was shifted downfield to 4.68 ppm, and the doublet centered at 5.08 ppm became a multiplet centered at 5.19 ppm. These changes are consistent with increased amounts of threo isomers, which would lead to the observed downfield shifts in both the α-H and β-H (see ref 14). Table III compares the chemical shifts for α-H and β-H for these various polymers and presents the ratios of erythro/threo isomers observed for the various conditions investigated. The equilibrium constants for the formation of erythro/threo isomers in the presence of TBAH or NaOH lead to the $\Delta\Delta G°$ of ~6 kJ/mol, from TBAH to LiOH a $\Delta\Delta G°$ of ~10 kJ/mol, a small energy difference for the two isomers.

Assuming that each polymer chain contains only one free phenolic group, it is possible to estimate the average molecular weights of some of the polymers prepared by using the ratio of the areas under the signals α-H and phenolic OH. As shown in Table I, despite large experimental errors, there is good agreement between the NMR results and those from HPSEC.

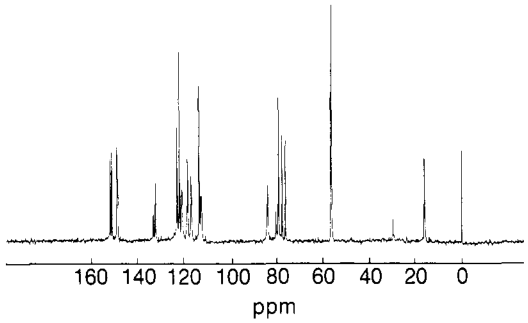


Figure 5. ^{13}C NMR spectrum of polymer prepared from quinonemethide (33 mM) in acetonitrile with aqueous sodium hydroxide. Polymer dissolved in $CDCl_3$.

Table IV
^{13}C NMR Chemical Shifts and Assignments of Polymers in Deuteriochloroform

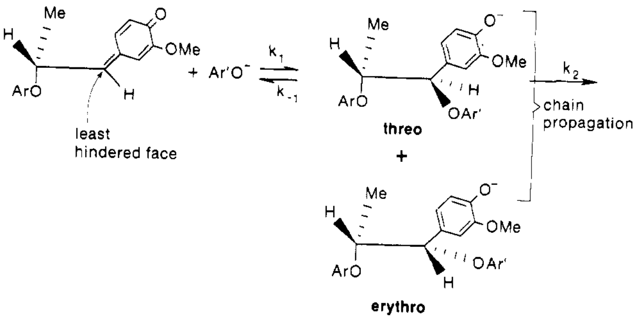
δ, ppm		
TBAH, EC	$NaOCH_3$	assignment
15.98	16.2	aliphatic CH_3
	55.2	aliphatic OCH_3
55.85	55.83	aromatic OCH_3
56.29	56.07	aromatic OCH_3
79.75	79.75	α-C (O–Ar substituted)
83.16	83.32	β-C (O–Ar substituted)
110.03		vw[a]
111.76	111.71	guaiacyl C-2
112.63	112.52	guaiacol C-2
113.98		vw[a]
115.93	115.99	guaiacyl C-5
117.88	117.39	guaiacol C-5
119.89	119.99	guaiacyl C-5
120.86	120.86	guaiacol C-1 and C-6
122.11	121.89	
123.25		vw[a]
130.72	131.21	vw[a]
132.19	132.19	guaiacyl C-1
145.24	147.68	vw, guaiacyl C-4, free phenolic
147.57	147.95	guaiacol and guaiacyl C-3
149.96	149.95	guaiacyl and guaiacol C-4 (aryl etherate)
150.93	150.78	guaiacyl and guaiacol C-4 (aryl etherate)

[a] vw = very weak.

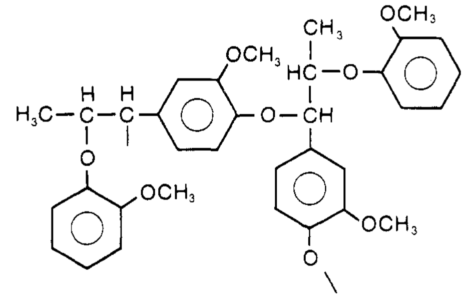
As in the case of the ^1H NMR spectra, the ^{13}C NMR spectra of the polymers generated with TBAH and EC are also very similar (see Figure 5 for an example). The sharp lines observed suggest that the polymers are regular and highly symmetrical. The chemical shifts and their corresponding assignments are listed in Table IV. Both the α-C and the β-C appear as one major signal at 79.75 and 83.16 ppm, respectively, both accompanied by small shoulders. These observations are in agreement with the ^1H NMR data, which indicate that the erythro configuration is predominant in these polymers.

The *O*-aryl-substituted α-carbons appear at 79.75 ppm (see Nimz et al.[15]), and the absence of signals at around 72 ppm indicates that there are very few free α-hydroxy groups. This is expected since HO^- initiators could be present only at the end of each chain. For instance, if the degree of polymerization is 8, $^1/_{135}$ carbon atoms would be attached to these groups, or $^1/_{24}$ α-carbon atoms, which would be difficult to detect in the ^{13}C spectrum. The presence of signals at 149.96 and 150.93 ppm also confirms the presence of guaiacyl-*O*-4-aryl etherate in the polymers. In the preparation of polymer with sodium methoxide, it is possible to detect a very small methoxy peak at 55.2 ppm with about 3%–4% of the overall methoxy carbon intensity. This signal can be assigned to the α-methoxy carbon,[16] confirming the nature of the initiator nucleophile in this case.

Scheme I
Polymerization Scheme



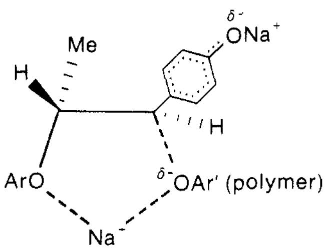
In agreement with the proposed Michael addition mechanism, the spectroscopic data confirm that the polymer has repeating units as follows:



Discussion

When base is added to the quinonemethide solutions, polymers are formed chemically involving reactions shown schematically in eq 1–4 above. In the nonaqueous solvents employed, primarily in the low dielectric constant solvent acetonitrile used in the preparation of the chemical polymers, ion-pair association between the cation and anions is favored.[17] Free phenolate anions and associated forms could participate in the Michael addition, as indicated by the differences in observed behavior when tetrabutylammonium and tetraethylammonium cations were present compared to when sodium and lithium cations were used.[18]

The growth of the polymer chain may be described by Scheme I, and it is seen that the stereochemistry of the linkage is established at each successive nucleophilic addition. According to Cram's rule,[19] attack of the nucleophile from the least hindered face of the sp^2 center will lead preferentially to the threo linkage; this is the product of kinetic control ($k_2 \gg k_{-1}$). Such predominantly threo product is observed in the synthesis of model dimer compounds from similar quinone methides.[20] In contrast, should the back reaction (k_{-1}) be faster, or comparable to the rate of chain propagation (k_2), then thermodynamic control will be established and the more stable erythro isomer will predominate. The fact that, in organic solvents, the sodium and lithium phenoxides are considerably more strongly ion-paired than the corresponding tetraalkylammonium salts[21] can alter the relative rates of k_{-1} and k_2. There is evidence[18,21,22] that in such cases ion pairs are the effective nucleophiles. Consequently, the sodium phenoxide (or lithium phenoxide) will attack as a unit and the transition state will resemble TS, in which chelation of the sodium ion is a stabilizing factor as the sodium ion pair dissociates. In concert with this will be the developing ion-pair stabilization at the 4-oxygen anion; this latter ion pairing will cause the back reaction (k_{-1}) to be slower than in the corresponding tetraalkylammonium case. Furthermore, the newly formed sodium (lithium) ion-paired phenoxide is the nucleophile for the next propagation step, and in turn its sodium (lithium) ion is involved in chela-



TS

tion. In this way, the necessary sodium (lithium) ion lability is maintained. The net result of these features is that in the presence of sodium (or lithium) ions kinetic control is favored (giving threo-rich polymers), whereas in the presence of tetrabutylammonium (or tetraethylammonium) ion thermodynamic control is more likely, giving erythro-rich polymer.

Conclusions

A number of lignin-model polymers have been prepared by addition of catalytic amounts of base to quinonemethides both chemically and electrochemically. These polymers are α,β-bis(*O*-4-aryl)ether bonded and have regular repetitive structures. Polymers have been produced in the range of 700–7000 apparent peak molecular weights. These polymers are stable in THF and other solvents. They are very useful as well-defined polymers, of known structure and with chemical functionalities that bear close resemblance to the isolated lignin polymers. These polymers are being further characterized for their absolute molecular weight and will be employed for the calibration of molecular weight distributions of lignin polymers in a variety of solvents.[23] Comparison between the behavior of these lignin-like polymers and polystyrene standards will be made. Polystyrenes are frequently employed but have been shown to be quite inadequate standards in more polar solvents such as DMF and DMF with LiCl or LiBr, which are excellent solvents for lignins.[11]

In the presence of tetraalkylammonium (alkyl = butyl and ethyl) cations, in both base-initiated and electrochemically initiated polymerization, the thermodynamically more stable erythro isomer is preferentially formed (ratio 4:1 for butyl and 2:1 for ethyl). The threo isomer is preferentially formed in the presence of alkali metal cations, and the ratio is reversed to 1:3 for sodium ions and to 1:10 for lithium ions. In energetic terms, this corresponds to a $\Delta\Delta G°$ of ~6 kJ/mol (tetrabutyl to sodium ions). Such a small difference can easily be explained in terms of conformational effects. An explanation based on the application of Cram's empirical rule concerning nucleophilic addition reactions combined with well-established template roles of alkali metal cations is proposed.

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Registry No. QM, 36382-85-1; QM (homopolymer), 110550-42-0; TEAP, 2567-83-1; TBAP, 1923-70-2; TBAH, 2052-49-5; NaOH, 1310-73-2; $NaOCH_3$, 124-41-4; LiOH, 1310-65-2.

References and Notes

(1) *Lignins: Occurrence, Formation, Structure and Reactions*; Sarkanen, K. V., Ludwig, C., Ed.; Wiley: New York, 1971.
(2) Gierer, J. *Holzforschung* **1982**, *36*, 43, 55 and references therein.
(3) Obst, J. R.; Landucci, L. L.; Sanyer, N. *Tappi* **1979**, *62*(1), 55.
(4) Holton, H. H. *Pulp Paper Can.* **1977**, *78*, T218. Fleming, B. I.; Kubes, G. J.; McLeod, J. M.; Bolker, H. I. *Tappi* **1978**, *61*(6), 43. Simard, G. L.; Genco, J. M.; Hendriksson, K. L., Jr. *Tappi* **1979**, *62*(5), 91. Samuelson, O. *Pulp. Paper Can.* **1980**, *81*(8), 68.
(5) Landucci, L. L. *Tappi* **1980**, *63*(7), 95. Gierer, J.; Lindeberg, O.; Noren, I. *Holzforschung* **1979**, *33*, 213. Aminoff, H.; Brunow, G.; Miksche, G. E.; Poppius, K. *Paperi Puu* **1979**, *61*, 441.
(6) Dimmel, D. R.; Shepard, D. *J. Org. Chem.* **1982**, *47*, 22; *J. Wood Chem. Technol.* **1982**, *2*, 73.
(7) Dimmel, D. R. *J. Wood Chem. Technol.* **1985**, *5*, 1 and references therein.
(8) Smith, D. A.; Dimmel, D. R., Proceedings of the 1985 International Symposium on Wood and Pulping Chemistry, Poster Session, Vancouver, Aug 26–30, 1985, p 39, presented at Tappi R+D Conference, Oct 1, 1986, Raleigh, NC.
(9) Dimmel, D. R.; Perry, L. F.; Palasz, P. D.; Chum, H. L. *J. Wood Chem. Technol.* **1985**, *5*, 15.
(10) Chum, H. L.; Johnson, D. K.; Palasz, P. D.; Schuller, L. F.; Dimmel, D. R., unpublished results.
(11) Chum, H. L.; Johnson, D. K.; Tucker, M.; Himmel, M. *Holzforschung* **1987**, *47*, 97–108.
(12) Ralph, J.; Young, A. *J. Wood Chem. Technol.* **1983**, *3*, 161.
(13) See Bergmann, E. D.; Ginsburg, D.; Pappo, R. *Org. React.* **1959**, *10*, 179.
(14) Zanarotti, A. *J. Chem. Res., Miniprint* **1983**, 2625.
(15) Nimz, H. H.; Tschirner, U.; Stahle, M.; Lehmann, R.; Schlosser, M. *J. Wood Chem. Technol.* **1984**, *4*, 265 and references therein.
(16) Chum, H. L.; Johnson, D. K.; Ratcliff, M.; Black, S.; Schroeder, H. A.; Wallace, K. Proceedings of the International Symposium on Wood and Pulping Chemistry, Vancouver, Aug 26–30 1985, Canadian Pulp and Paper Association, p 223.
(17) Szwarc, M. *Carbanions, Living Polymers and Electron Transfer Processes*; Interscience: New York, 1969. *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley: New York, 1973; Vol. I.
(18) Bethell, D.; Fairclough, C. S.; Wilkinson, R. G. *J. Chem. Soc., Perkins Trans. 2* **1975**, 1090. Bethell, D.; Cockerill, A. F.; Frankham, D. B. *J. Chem. Soc. B* **1967**, 1287. Bethell, D.; Fairclough, C. S.; Talbot, R. S.; Wilkinson, R. G. *J. Chem. Soc., Perkins Trans. 2* **1976**, 55.
(19) Cram, D. J. *Fundamentals of Carbanion Chemistry*; Academic: New York, 1964.
(20) Sarkanen, K. V.; Wallis, A. F. A. *J. Chem. Soc., Perkins Trans. 1* **1973**, 1869.
(21) Bethell, D.; Talbot, R. J. E. *J. Chem. Soc. B* **1968**, 638.
(22) Brandstrom, A.; Kolind-Andersen, H. *Acta Chem. Scand. B* **1975**, *29*, 201. Brandstrom, A. *Acta Chem. Scand. B* **1976**, *30*, 203.
(23) Chum, H. L.; Johnson, D. K.; Himmel, M.; Hyatt, J., unpublished results.