Table I
Calculated Conformationalharacteristics of Isolated n-Alkane Chains C_nH_{2n+2}

n	$\langle P_g \rangle^a$	$\langle N_g \rangle^a$	P_g(central)
5	0.450	0.090	
6	0.390	1.17	0.386
7	0.388	1.55	
8	0.392	1.96	0.405
9	0.393	2.36	
10	0.394	2.76	0.402
11	0.396	3.17	
12	0.397	3.57	0.403
13	0.397	3.97	
14	0.397	4.37	0.402
15	0.398	4.77	
16	0.398	5.18	0.402
17	0.399	5.58	
18	0.399	5.98	0.402
19	0.399	6.38	
20	0.399	6.79	0.402
21	0.399	7.19	
22	0.399	7.59	0.402

[a] Calculated only for the $n - 3$ internal bonds connecting methylene groups (CH_2) whose rotational states affect the shape of the chain molecule.

The average probability and number of gauche bond rotations and the probability that the central bond is in a gauche state calculated for the n-alkanes C_5–C_{22} are presented in Table I. There is clearly no evidence from the results calculated for isolated n-alkane chains to support the interpretation of Champion and co-workers[1,2] that a significant and abrupt change in their conformational characteristics occurs between the C_{12} and C_{14} members. For this reason and barring any peculiar interchain interactions which are fundamentally different for chains of 12 and 14 carbon atoms, we have serious reservations about their interpretation.

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Copolymerization of Methyl Acrylate with 1,1-Diphenylethylene. Effect of Concentration on Composition

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Received February 13, 1975

The bulk copolymerization of methyl acrylate (MA) (M_1) and 1,1-diphenylethylene (DPE) (M_2) has been investigated by Doak and Dineen[2] and Ito and Yamashita.[3] The latter investigators reported deviations in copolymer composition and sequence distribution from the terminal model[4] and better agreement with the penultimate model.[5] Litt and Seiner[6] used the terminal-complex model[7] to interpret these results.

In this study, the copolymerizations of MA and DPE in bulk and in cyclohexane solutions are investigated and the effects of the total monomer concentration, $[M^0] = [M_1^0] + [M_2^0]$, on the copolymer composition are reported. Terminal, penultimate, terminal-complex, and depropagation[8] copolymerization models are considered.

Experimental Section

Materials. The methyl acrylate, bp 80 °C,and the diphenylethylene, bp 123–125 °C (5 Torr),[9] were distilled just prior to use. The cyclohexane was spectrophotometric grade. The trifluoroacetic acid (TFA) was reagent grade and the benzoyl peroxide was used as supplied (Eastman Chem. Co.).

Polymerizations. Polymerizations proceeded homogeneously in evacuated, sealed ampules at 80.0 ± 0.1 °C with 0.1–0.2% benzoyl peroxide catalyst. Feed ratios, $x = [M_1^0]/[M_2^0]$, of 1 to 18 were used for polymerizations carried out in bulk and in cyclohexane solutions, with $[M^0] = 5.4$, 2.7, and 1.35 M. Polymerizations were terminated at conversions less than 6%. The product was precipitated with 60/90 petroleum ether, filtered, washed with ethanol, air-dried, dissolved in benzene, filtered, freeze-dried, and dried to a constant weight at 100 °C.

Spectra. The ^1H NMR spectra of the copolymers were determined at 75 to 85 °C with a 90 MHz Bruker HX-90, using filtered 15% (w/v) TFA solutions in sealed tubes. The TFA also provided the internal fluorine lock. Spectra of one sample were obtained over a period of 1 week without change. No impurity peaks were observed in a blank TFA sample subjected to the sample preparation procedures. Spectra run with CCl_4 as solvent gave values of the mole ratio of MA/DPE in the copolymer, $y = m_1/m_2$, within the experimental limits observed with TFA as solvent. Chemical analysis (Galbraith Laboratories) of six samples gave values of y within these same limits.

Two absorption regions occur in the ^1H NMR spectra: region A centered at 7.3 ppm with respect to TMS representing the phenyl protons and a broad region B extending from 4.0 to 0.7 ppm representing the remaining protons.[3] The protons of M_2 are represented by area A and the $A/5$ portion of area B. Correction for 12 protons in M_2 units compared with six in M_1 units yields, $y = (5B - A)/3A$.

Three spectra were obtained for each sample. Each spectrum was integrated three times with a planimeter to determine an average area and an average value of y was calculated for the sample. The standard deviations in the mole fraction of DPE in the copolymer F_2 were generally less than ±0.01, where $F_2 = (1 + y)^{-1}$.

Results and Discussion

Values for F_2 and f_2, $f_2 = [M_2^0]/[M^0]$, at various $[M^0]$ are listed in Table I. Figure 1, a graph of F_2 vs. f_2, shows the small, but orderly and measurable, effect of $[M^0]$ on the (F_2, f_2) dependence. F_2 increases with increasing $[M^0]$ for $f_2 < 0.14$ and decreases with increasing $[M^0]$ for $f_2 > 0.14$, with an isocomposition point at $f_2^0 = 0.14$.

Two factors complicate the interpretation of the concentration effect in terms of the copolymerization models: the effect is small and the dielectric constant of the medium changes with both $[M^0]$ and f_2. Despite these limitations, it is instructive to examine the applicability of these models in interpreting the concentration dependence of the copolymer composition and to compare the results of this study with those previously reported for bulk polymerizations. The terminal and penultimate models do not explicitly include concentration effects, although for a given $[M^0]$ both may be applied.

Homopolymerization of DPE was not observed under the reaction conditions and the terminal model was used in the form $y = 1 + r_{12}x$, where $r_{12} = k_{11}/k_{12}$ and $r_{21} = k_{22}/k_{21} = 0$. The values for r_{12} calculated using a linear least-squares procedure are given in Table II. The result for the bulk polymerization is in reasonable agreement with previous results at 60 °C; $r_{12} = 0.102 \pm 0.006$[2] and 0.092 ± 0.010.[3] Removal of

Table I
Mole Fraction of M_2 in the Copolymer (F_2) and in the Reacting Solutions (f_2) (Copolymer Ratio y and Feed Ratio x)

Total monomer concn in feed, $[M^0]$, M	F_2 (m_2)	f_2 ($[M_2^0]/[M^0]$)	y (m_1/m_2)	x ($[M_1^0]/[M_2^0]$)
Bulk: 10.36	0.28	0.060	2.61	15.6
10.54	0.30	0.064	2.32	14.6
10.22	0.33	0.077	2.05	12.0
9.99	0.36	0.101	1.81	8.86
9.57	0.38	0.143	1.62	5.99
8.90	0.42	0.249	1.37	3.02
5.40 ± 0.05	0.24	0.052	3.14	18.2
	0.26	0.060	2.89	15.6
	0.30	0.078	2.29	11.9
	0.35	0.100	1.82	8.96
	0.37	0.142	1.70	6.06
	0.45	0.243	1.23	3.11
	0.49	0.490	1.03	1.04
2.70 ± 0.05	0.24	0.052	3.11	18.2
	0.26	0.068	2.86	16.4
	0.30	0.078	2.36	11.9
	0.34	0.100	1.96	8.96
	0.38	0.142	1.63	6.06
	0.45	0.243	1.25	3.11
	0.49	0.490	1.05	1.04
1.35 ± 0.02	0.22	0.052	3.47	18.2
	0.25	0.060	2.98	15.6
	0.29	0.078	2.49	11.9
	0.33	0.100	2.07	8.96
	0.38	0.142	1.61	6.06
	0.46	0.243	1.17	3.11
	0.50	0.490	1.00	1.04

Table II
Reactivity Ratios in the Terminal Model

Concn, M	r_{12}	Standard deviation
(Bulk)	0.095	0.008
5.40	0.113	0.007
2.70	0.113	0.004
1.35	0.127	0.008

Table III
Reactivity Ratios in the Penultimate Model

Concn, M	r_{12}	r_{12}'	Stadard deviation
(Bulk)	0.089	0.103	0.007
5.40	0.149	0.076	0.006
2.70	0.137	0.084	0.001
1.35	0.149	0.096	0.008

the restriction $r_{21} = 0$ produced a stronger dependence of r_{12} on $[M^0]$, but the r_{21} were unreliable because data for $x < 1$ were not available. The extremely slow reaction rate at $x < 1$ limited the experimental range and prohibited optimization of the feed ratios.[10]

The penultimate copolymerization equation with $r_{21} = r_{21}' = 0$ is eq 1.[5]

$$y = 1 + r_{12}'(1 + r_{12}x)/(1 + r_{12}'x) \qquad (1)$$

A curve-fitting procedure minimizing the standard deviation between experimental points and curves calculated with eq 1 produced the results in Table III. Ito and Yamashita[3] reported $r_{12} = 0.065 \pm 0.005$ and $r_{12}' = 0.12 \pm 0.01$ for the bulk polymerization at 60 °C.

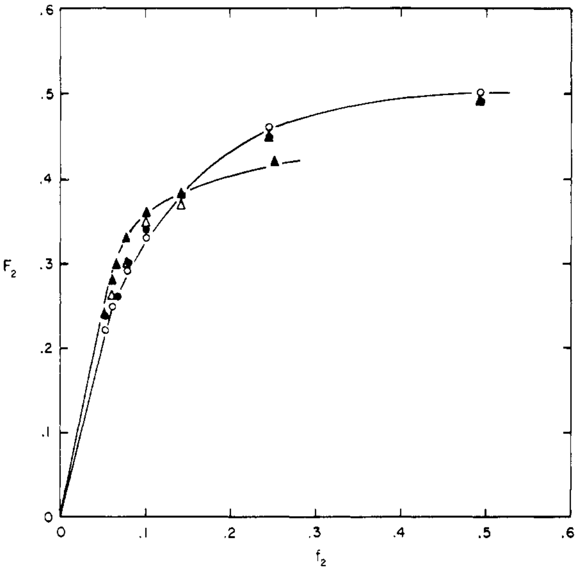

Figure 1. Mole fraction of DPE in the copolymer (F_2) vs. mole fraction in the feed (f_2): (○) $[M^0]$ = 1.35 M; (●) $[M^0]$ = 2.70 M; (△) $[M^0]$ = 5.40 M; (▲) bulk.

A depropagation model developed by Lowry[8] employing the usual terminal propagation steps and the reversible step, $(m_2\cdot)_n + M_2 \rightleftharpoons (m_2\cdot)_{n+1}$, with rate constants k_{22} and k_{22}', was examined for consistency with the results. The copolymerization equation predicts the F_2 dependence on f_2 to be an increasing function of $[M^0]$ for $0 < f_2 < 1$, with no isocomposition point.

Chain transfer to solvent is not expected to affect the chemical composition of the copolymer appreciably. The major effect, if realized, would be the reduction in the degree of polymerization.[11] However, no decrease in the viscosity of the samples prepared for the ^{1}H NMR experiment was observed for those copolymers polymerized in solution. A chain-transfer effect should either increase or decrease F_2 over the entire range of f_2.

Litt and Seiner[6] used the equation

$$(y - 1 - r_{1c}/r_{1c1})[M_2^0] = r_{1c}/K - (r_{1c}/Kr_{12})(y - 1)/x \qquad (2)$$

in applying the terminal-complex model to the bulk polymerization results of Ito and Yamashita,[3] where $K = [C]/[M_1][M_2]$, $r_{12} = k_{11}/k_{12}$, $r_{21} = k_{22}/k_{21} = 0$, $r_{1c} = k_{11}/(k_{1c1} + k_{1c2})$, $r_{1c1} = k_{11}/k_{1c1}$, and $r_{2c1} = k_{22}/k_{2c1}$. Equation 2 is derived assuming DPE does not self-propagate and K is small. Values for r_{1c}/r_{1c1} were selected until a straight-line plot of $(y - 1 - r_{1c}/r_{1c1})[M_2^0]$ vs. $(y - 1)/x$ was produced.

Application of this procedure to the solution polymerizations gave straight-line plots but with a different positive slope for each $[M^0]$. These results are inconsistent with the model; a positive slope has no physical interpretation and the slopes should be independent of $[M^0]$. In addition, no complex could be detected by either ^{1}H NMR or uv spectroscopy of solutions containing mixtures of the monomers.[12]

Despite the lack of agreement with the terminal-complex model, it should be emphasized that the model is consistent with two characteristic features of the dependence of (F_2, f_2) on $[M^0]$: the terminal-model r_{12} values increase with dilution,[7] and an isocomposition point occurs within the limits of the model.[13]

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Simulation of Reactions with Lignin by Computer (SIMREL). 5. Nondehydrogenative Polymerization in Lignin Formation

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Received March 29, 1976

In previous papers of this series,[2] two of us have reported on computer simulation studies of the formation and analysis of softwood lignin.In the last two papers it was demonstrated that the computation of model structures is not possible, which satisfy all experimental results of the elemental analysis, ^1H NMR spectroscopy, and oxidative degradations with nitrobenzene and permanganate, unless the concentration of linkages based on nondehydrogenative polymerization reaches levels of 22–24% of the total number of linkages. The existence of such linkages in lesser concentrations has been known for some time, and has commonly been reported to occur in the form of benzyl aryl ethers (α-O-4) (Type A, Figure 1).[3] However, when all nondehydrogenative linkages in lignin were assumed to be of the α-O-4 type in the simulation, we did not succeed in modeling a lignin structure which could duplicate analytical observations. Experimental and modeled analytical results deviated to a lesser degree if ¾ of all nondehydrogenative linkages were of a benzyl alkyl ether, α-O-γ type (B, Figure 1). In this event, however, modeling consistently required the presence of upwards to 30% double bond containing end groups, an observation which was incidenced by the necessity to limit the abundance of pinoresinol type, β–β linked structures to 2–4%. Such low concentrations of pinoresinol structures in spruce lignin are indicated by the carbon-13 nmr spectra,[4] and have previously been concluded from the absence of pinoresinol among the acidolysis products of spruce lignin.[5] If constraints were introduced in the simulation program to limit the number of end groups to 9%, the value cited by Lai and Sarkanen,[6] dehydrogenative simulated polymerization did not progress. Even lower endgroup concentrations (6%) were quoted in two Swedish publications.[7] This observation led two of us (W.G.G. and H.R.G.) to the conclusion that some kind of vinyl polymerization must occur during the formation of lignin, which leads to nondehydrogenative linkages by involving double bonds.[8] Recent experimental evidence obtained by one of us (H.H.H.N.) provides support for the occurrence of vinyl-type polymerization in lignin through the successful isolation of α–β linked dimers from beech and spruce lignin.[9] We have now jointly explored, by computer simulation, the impact which the presence of several mechanistically conceivable, vinyl-based nondehydrogenative linkages would have on a model lignin structure in terms of expected analytical results. These simulations have resulted in several model structures among 80, which can explain analytical results obtained by elemental analysis (procedure I), ^1H NMR spectroscopy (procedure II), nitrobenzene oxidation (procedure III), permanganate oxidation (procedure IV), and permanganate oxidation following mild alkaline hydrolysis (procedure V). The best of these structures has an empirical formula of $C_9H_{7.11}O_2(H_2O)_{0.41}(OCH_3)_{0.92}$ reflecting a degree of dehydrogenation (DD) of 1.98. Results obtained by Freudenberg and co-workers following extensive structural work of softwood lignin indicate that lignin of spruce wood has the composition of $C_9H_{7.15}O_2(H_2O)_{0.40}(OCH_3)_{0.92}$ and a DD of 1.94.[10] Simulated analytical results of procedures I–V show similar accord with experimental values. Some of them are as follows (experimental values given in parentheses; for reference see papers III and IV of this series[2] and Miksche et al.[11]): Procedure I (in %): C, 65.03 (65.08); H, 5.88 (5.90); O, 29.09 (29.02). Procedure II (acetylated lignin, in H/C_9): aromatic and α-vinylic, 2.7 (2.6); acetoxyl, 4.2 (4.2). Procedure III (yield in %): vanillin, 37.1 (27.5). Procedures IV/V (all as methyl esters, yield in %): veratric acid, 14.8/35.3 (10.6/29.8); isohemipinic acid, 4.4/11.8 (1.9/5.0); metahemipinic acid,[13] 1.5/4.4 (0.8/1.1); 2,2′,3,3′-tetramethoxybiphenyl-5,5′-dicarboxylic acid, 0.0/6.8 (1.1/6.7); 5-(2-methoxy-4-carboxyphenoxy)veratric acid, 2.2/4.4 (1.5/2.1). This lignin model structure is based on a total of 23.4% nondehydrogenative linkages and 8.5 and 4.3% sidechain displacement and phenol dienone rearrangement reactions, respectively (cf. paper I of this series).[2] The concentration of double bond-containing end-groups is 12%, that of phenolic hydroxyl groups 30%, and that of β-β linkages 2.1%.

Nondehydrogenative linkages contained in this model structure are of five different types, and these are shown in Figure 1. The relative frequencies of these linkages amount to: types A (α-O-4) and B (α-O-γ) 25% each, types C (α-β, 6-α; indan) and D (α-β) 15% each, and type E (α-β, γ-O-α; pyran) 20%.

The formation of type C–E structures can be explained through cationic vinyl polymerization involving benzylium ions. A related effect of the natural acidity of cell saps on coniferyl alcohol has earlier been suspected by Freudenberg, Maercker, and Nimz,[12] who thought that the H^+ concentration at the cell boundaries may influence tree lignification. In this study, coniferyl alcohol was polymerized at pH 2.5–3, and dimeric and trimeric structures similar to the ones proposed here were isolated. However, the suspected presence of such structures in native lignin has later been abandoned.

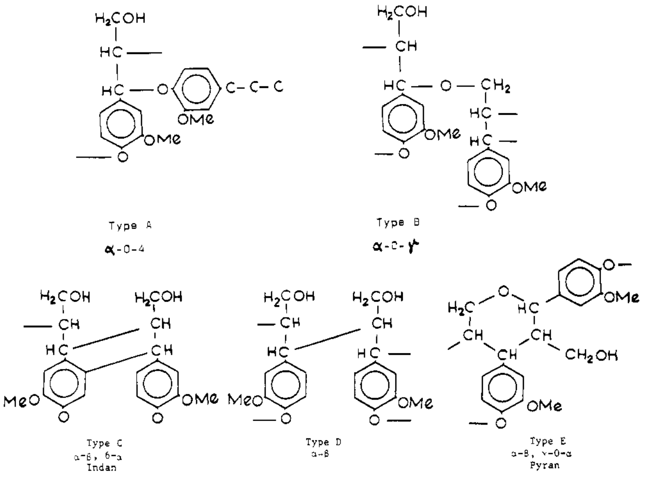

Figure 1. Proposed nondehydrogenative linkages in lignin.

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