is a higher energy form relative to the antiparallel cellulose II. Presumably, the kinetics of biosynthesis are such that crystallization is either favored or faster than chain folding which otherwise would lead to an antiparallel structure. The chains crystallize into strongly hydrogen bonded sheets which lend cellulose its characteristic strength, yet the bonding between sheets is not strong, permitting structural flexibility necessary for plant cell walls and their growth. When a hydrogen bond breaker, such as ammonia, acts on cellulose I, all hydrogen bonds are probably broken and the structure rearranges into another least energy form that may be an ammonia complex. Because the cellulose chain is stiff and the ammonia treatment is not sufficiently drastic to solubilize the structure, chain folding does not occur in this complex. Upon evaporation of the ammonia, the cellulose structure reforms its intrasheet hydrogen bonds but settles into the nearest energy minimum which is cellulose $\mathrm{III_I}$, retaining the parallel structure but showing a shift of sheets relative to the structure of cellulose I. Because the latter resides in a global minimum for parallel structures,[7] a supply of some energy to $\mathrm{III_I}$ results in its reversion to I. This process need not be a high energy one because hydrogen bond breaking is not needed in the shift of adjacent sheets. Although little is known about cellulose $\mathrm{IV_I}$ which can be made from $\mathrm{III_I}$ (or cellulose I) by high temperature heating in the solid state, the chances are good that it is also a parallel chain structure.

On the other hand, when cellulose I is solubilized and subsequently regenerated, the chains may fold[14] and seek out the true global minimum for cellulose crystal structures, the antiparallel cellulose II. The latter can also form an ammonia complex, because of the general similarity of parallel and antiparallel cellulose structures. This complex, however, results in an antiparallel cellulose $\mathrm{III_{II}}$ which is metastable with respect to II and reverts to the latter in the same fashion as $\mathrm{III_I}$ reverts to I. Again, on the strength of similarities in structures, there probably exists a $\mathrm{IV_{II}}$ which is antiparallel. Because the differences in the structures of $\mathrm{III_I}$ and $\mathrm{III_{II}}$ reside mainly in chain polarity, as is true of the structures of I and II, the solid state conversions of II to I and $\mathrm{III_{II}}$ to $\mathrm{III_I}$ cannot occur.

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Supplementary Material Available: Tables I, IV, and VII (5 pages). Ordering information can be found on any current masthead page.

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Notes

Comments on the Liquid State Conformations of *n*-Alkanes

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Recently Champion and co-workers,[1,2] in attempting to account for molecular weight anomalies observed in their flow birefringence and laser light-scattering studies of liquid *n*-alkanes, proposed that an abrupt change in the conformational characteristics occurs between the C_{12} and C_{14} members of this homologous series of liquids. To explain the differences in the temperature dependence of the flow birefringence[1] and the low frequency depolarized spectra of scattered light[2] they observed between the smaller ($\leq C_{12}$) and larger ($\geq C_{14}$) *n*-alkane liquids, Champion and co-workers suggested[1,2] that the C_{12} and lower members exist predominantly in the all-trans, planar zigzag conformation, while the C_{14} and higher homologues experience a sudden increase in their gauche rotational state populations which results, on the average, in their possessing one more gauche bond than the smaller *n*-alkanes.

In an effort to determine whether or not their suggestion of a sudden conformational transition between the C_{12} and C_{14} members of the liquid *n*-alkanes has an inherent intramolecular origin, rotational isomeric state (RIS) calculations[3] are performed on isolated C_5–C_{22} *n*-alkane chains to determine the average probability $\langle P_g \rangle$ and number $\langle N_g \rangle$ of gauche bond rotations possessed by each and the probability P_g(central) that the central bond in each of the even members (C_6, C_8, C_{10}, . . . , C_{22}) is in a gauche rotational state.

The usual three-state RIS model[3] (trans and two gauche states) appropriate to *n*-alkanes and polyethylene is adopted. Each gauche rotational state incurs an energy cost of 500 cal/mol relative to the trans state and an additional 2.0 kcal/mol when it occurs paired with an adjacent gauche rotational state of the opposite sign. This RIS model has been successful in predicting the dilute solution dimensions and their temperature dependence[4] and the constant volume entropy of fusion[5] of polyethylene, the depolarized light scattering of dilute *n*-alkanes,[6] the dipole moments of the terminally substituted dibromo-*n*-alkanes[7] ($\mathrm{Br(CH_2-)}_n\mathrm{Br}$), and the dimensions of neat terminally halogenated *n*-alkanes.[8,9] All calculations were performed at 140 °C using the matrix multiplication methods described by Flory.[3]

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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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