Table I
Polymerization of 2-MOCB with Modified $(i\text{-Bu})_3Al$ Initiators[a]

added per mole of $(i\text{-Bu})_3Al$	temp, °C	time, h	polymer yield, wt %	$\overline{M}_n{}^b \times 10^{-3}$	$\overline{M}_w{}^b \times 10^{-3}$	$[\eta]$,[c] dL/g
0.5 H_2O[d]	0	45	92	12	38	0.35
0.5 H_2O	−78	120	67	210	475	3.7
0.67 H_2O	60	49	94	4	16	
0.67 H_2O	−30	0.25	45	33	147	
0.67 H_2O[e]	−30	88	72	74	185	2.6
1.0 H_2O	−30	25	86	57	145	
0.5 H_2O, 0.5 Acac	30	266	41	40	770	
0.5 H_2O, 0.5 Acac	0	1107	0.9			
0.5 H_2O, 0.5 Acac	−30	138	0.8			
0.4 H_2O, 0.8 Acac	30	843	60	290	895	6.9
0.5 H_2O, 1.0 Acac	30	721	37	300	970	
1.0 H_2O, 0.5 Acac	30	836	1.9			

[a] Polymerizations carried out in *n*-heptane solution under the following conditions (unless otherwise indicated): concentration of monomer, 3.4 mol L^{-1}; concentration of initiator ($(i\text{-Bu})_3Al$ basis), 0.07 mol L^{-1}. [b] Determined by gel permeation chromatography in THF. [c] Intrinsic viscosity was measured in chloroform at 25 °C. [d] Concentration of monomer, 7.5 mol L^{-1}; concentration of initiator, 0.15 mol L^{-1}. [e] Concentration of monomer, 1.0 mol L^{-1}; concentration of initiator, 0.02 mol L^{-1}.

with the previous assignment of the signals.[1] It is noted that the triplet signals at 72.6, 72.7, and 72.8 ppm arising from the methine carbons in the stereochemical triads in the head-to-tail structures appear in intensity ratios very close to 1:2:1, indicating randomness of the configuration and no stereoselection by the applied initiator. The spectra 1b and 1c of the polymers prepared with the coordination initiators clearly indicate the absence of head-to-head, tail-to-tail structures as found also by Oguni and Hyoda for the polymer prepared with their initiator. Interestingly, we find, however, a marked shift in the intensity distribution of the triplet signals, appearing at the same positions as in spectrum 1a from the triad structures, being 1:1:1.2 in the case of 1b and 1:1.2:1.6 in the case of 1c. Therefore, the distribution of the chiral carbons is not random in the polymers prepared with the coordination initiators. Thus these initiators are able to exert an influence on the stereochemistry of the propagation. It is seen that the signal at 72.8 ppm arising from the syndiotactic triad, as already assigned to the lowest field,[2] grows in intensity at the expense of the signals from the heterotactic and isotactic triads. This effect appears to be accentuated by increasing the amount of acetylacetone in the initiator. However, as already pointed out, this amount must be limited.

In the case of the cationic polymerization of 2-MOCB, stereospecificity is not found because both of the oxygen–carbon bonds in the cyclic oxonium ion may open in the propagation step, and it appears that the chain end is not able to exert a controling influence during the propagation of this monomer. Vandenberg found[5,6] with this type of cationic initiator that tactic polymers could be obtained in the case of the disubstituted epoxides *cis*- and *trans*-2,3-epoxybutane, since with these monomers a chain end interaction with the oxonium ion causes the ring opening to take place in a specific manner or an enantiomeric selection takes place during the process. in the case of the coordination polymerization of 2-MOCB the basic condition for obtaining head-to-tail polymers is fulfilled, namely, that the bond breakage in the cyclic propagating intermediate occurs in a specific manner. The coordination complex also has some ability to select between the two enantiomeric forms of the monomer, yielding a less than random proportion of heterotactic structures. The nature of this controlling influence, however, has not been investigated, and it is not known presently if the polymers produced are homogeneous with respect to stereochemical distribution.

Experimental Section

Materials. The monomer 2-MOCB was prepared as previously described.[1] Triisobutylaluminum (Fluka, practical grade) was used as received. *n*-Heptane was distilled and was more than 99.5% pure as determined by gas chromatography. Acetylacetone (Merck, synthesis grade) was distilled prior to use.

Initiator Preparation. The preparations were carried out in a glovebox by adding water to a solution of $(i\text{-Bu})_3Al$ in *n*-heptane at 0 °C under magnetic stirring. In the case of the preparation of the coordination initiator, acetylacetone was subsequently added after 30 min (0 °C). The solutions were stirred for 24 h at room temperature prior to use.

Polymerization Experiments. All polymerizations were carried out by using standard high-vacuum techniques. The initiator solutions were added with a syringe to the polymerization ampules. The polymerizations were terminated by addition of ethanol containing concentrated hydrochloric acid. The solutions were subsequently washed with 1 N sodium hydroxide and water.

Characterization of Products. Molecular weights were determined by gel permeation chromatography (Waters Model 200) using THF solvent and polystyrene gel columns with porosities 10^6, 2×10^4, 10^4, and 10^3 Å. The molecular weight values were calculated on the basis of a calibration curve obtained with narrow molecular weight samples of polystyrene from Water Associates. The calculations were based on the principle of extended chain lengths applying a *Q* value (weight per Å) of 15.4. The ^{13}C NMR spectra were obtained in deuteriochloroform at room temperature with tetramethylsilane as internal reference on a Bruker HX270 FT spectrometer operating at 67.89 MHz.

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Decalin Ring Structures in the Products of BF_3-Catalyzed Oligomerization of Cyclopentene

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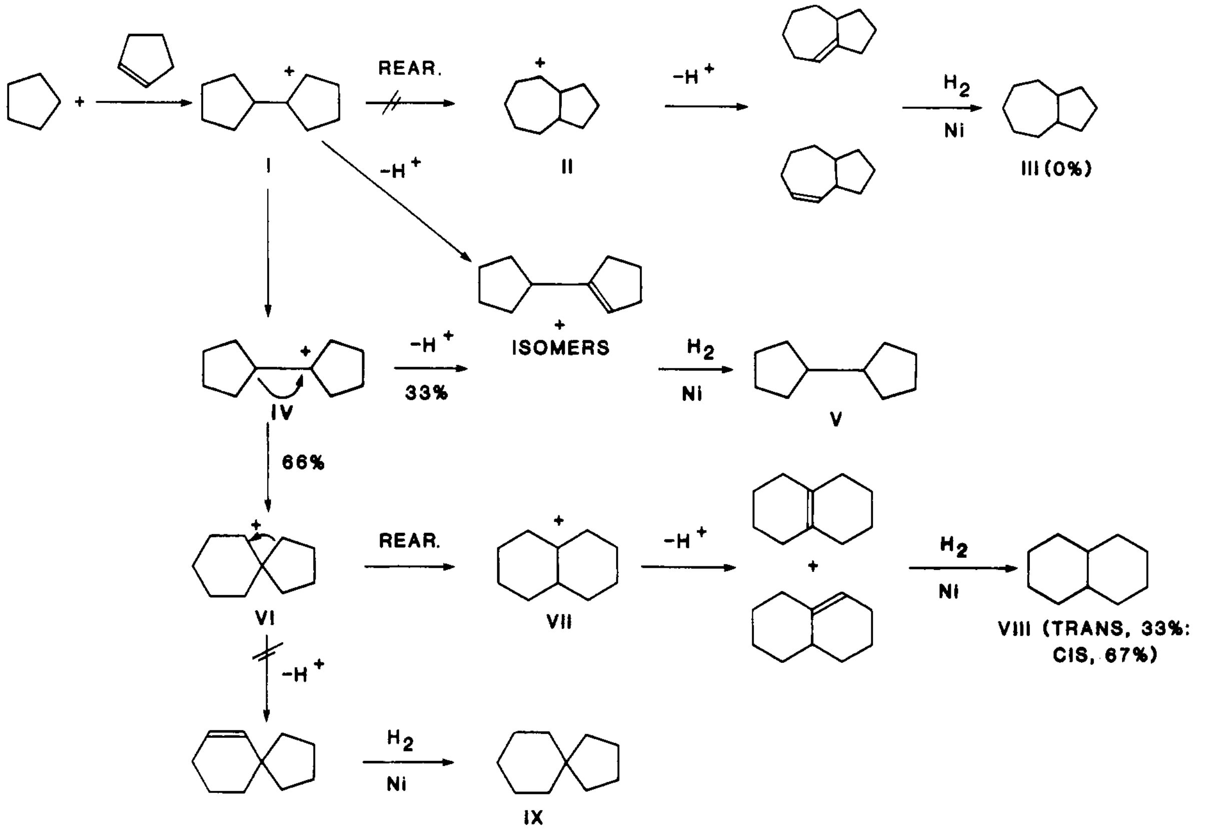
Cationic polymerizations of alkenes are commercially important processes for the preparation of widely used

Scheme I
Reaction Pathway for Oligomerization of Cyclopentene



polymers. Two excellent texts are available on the subject.[1,2] While much information is available on the products of the polymerization of simple alkenes such as propylene and isobutylene, relatively little is known about the structure of products derived from cyclics.

We were interested in the oligomerization of cyclopentene and cyclohexene with BF_3 complexes. The literature on this subject was very limited. For example, depending on the alkene and the catalyst, the alkenes polymerize either (1) across the double bond, (2) with ring opening to give cis and/or trans polymers, or (3) both. Boor et al.[3] reported that Ziegler catalyst ($TiCl_3$ and $AlEt_3$) and a cationic vanadium system (VCl_4 and $AlMe_2Cl$ or $AlMe_3$) both polymerized cyclopentene, while $AlCl_3$ was ineffective. The authors concluded that cyclopentene formed polymers resulting from both the polymerization across the double bond and ring-opening processes. None of the catalysts studied were effective with cyclohexene.

In contrast, Rudenko and Gromova[4] reported that the polymerization of cyclopentene with $AlCl_3$ (20% $AlCl_3$, 50 °C, 30 h) afforded the corresponding oligomers. The dimer fraction was identified largely as the saturated spiro[4.5]decane.

Hofmann[5] mentioned in his progress report that he polymerized both cyclopentene and cyclohexene with BF_3 (HF promoter) and obtained dimers, trimers, tetramers, and still higher distillable oligomers, but the experimental conditions and analytical data were not given.

Natta et al.[6] treated cyclopentene with cationic WCl_6 and obtained only a small amount of oil after 24 h of reaction. The same catalyst in the presence of $AlEt_3$ converted cyclopentene into essentially pure *trans*-polypentenamer.

Finally, Nametkin and Rudenko[7] treated cyclohexene with $AlCl_3$ (5–10% $AlCl_3$, 70–80 °C, 30 h) and found among the oligomers a considerable amount of saturation. One of the hydrocarbons was identified as tetracyclohexylbenzene.

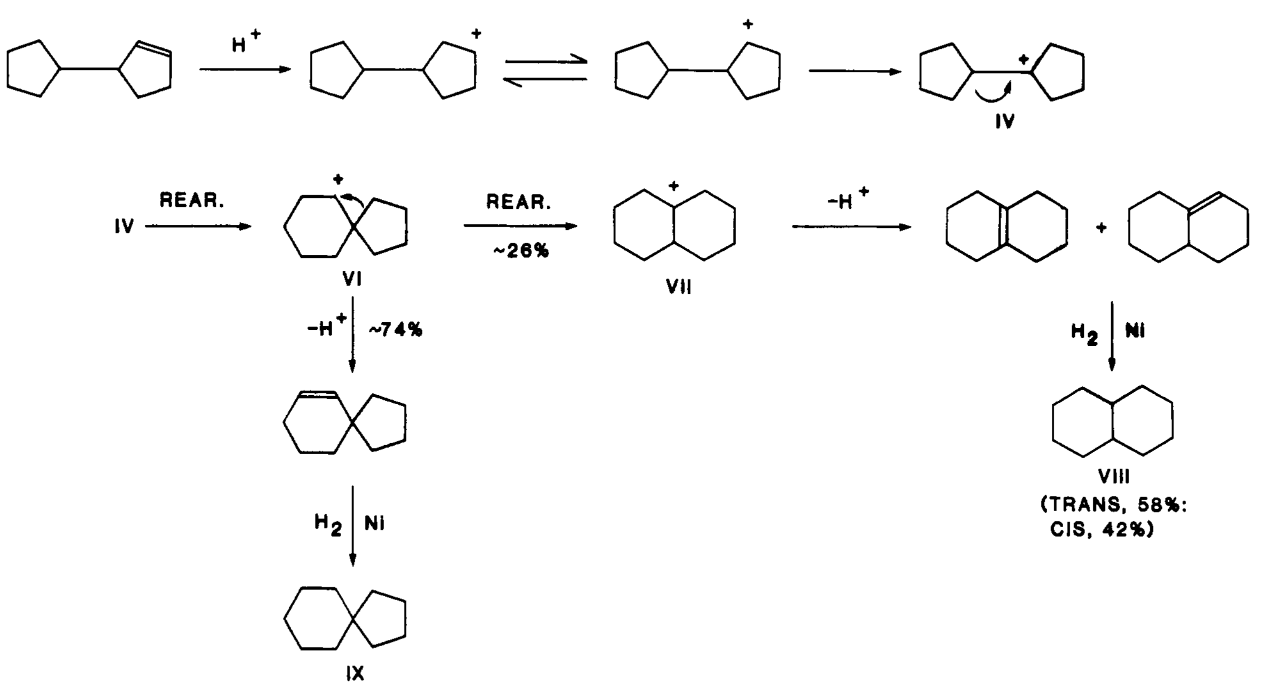
Discussion

Recently, Cesca et al.[8,9] reported on the structure of products resulting from the cationic polymerization of propylene and 1-butene. Using ^{13}C NMR, they identified 11 distinct structural groups, but no predominant isomerization pathway was evident. This finding suggested to us that during the oligomerization of cyclic alkenes, some isomerization in the way of ring contraction and ring expansion should be present in addition to the usual reactions across the double bond and ring opening, but this isomerization has not been demonstrated.

In this study, cyclopentene and cyclohexene were oligomerized with BF_3, with 1-butanol as the cocatalyst. The products were oligomeric, with the degree of polymerization n being ~2–6. Analysis of the original products by ^1H and ^{13}C NMR indicated the absence of aromatic structures and products from ring-opening reactions. Hence, the cyclic structures were preserved in the BF_3 system. To simplify the analysis, the reaction mixture was hydrogenated, and the analysis of the saturated hydrocarbon mixture thus obtained was performed by GLC after the product had been separated into its respective oligomer fractions by distillation. In this manner, the products from the ring expansion, those from ring contraction, and those from the unrearranged skeleton could most readily be established.

The hydrogenated dimer fraction from the cyclopentene reaction was found to consist of *trans*-decalin (22%), bicyclopentyl (33%), and *cis*-decalin (44%). The results of oligomerization of cyclopentene are explained according to Scheme I. Following the protonation of cyclopentene, the cyclopentyl carbenium ion adds to a second cyclopentene to give ion I. Ion I can rearrange to ion II, but

Scheme II
Reaction Pathway for Isomerization of 3-Cyclopentylcyclopentene



this rearrangement did not appear to take place since none of the bicyclo[5.3.0]decane (III) was detected among the products. Ion I can undergo deprotonation to form alkenes, but apparently it first rearranges to a more stable ion IV, which eventually will give bicyclopentyl (V). Ion IV apparently also rearranges to the spiro[4.5]decyl ion VI, which then further rearranges to VII and results in the decalin ring structure. Ion IV on deprotonation was expected to give some spiro[4.5]dec-1-ene, but none of this alkene was detected.

In a control experiment 3-cyclopentylcyclopentene, when treated with BF_3 under the reaction conditions, was isomerized to a mixture of octalins (26%) and spiro[4.5]dec-1-ene (74%), which on hydrogenation resulted in *cis*-decalin (11%), *trans*-decalin (15%), and spiro[4.5]decane (74%), supporting the proposed rearrangement mechanism (Scheme II).

The basic difference between the products of cyclopentene oligomerization (Scheme I) and those of 3-cyclopentylcyclopentene isomerization (Scheme II) is the predominance of the spirodecane ring formation in the latter with only little oligomerization. This difference can be explained on the basis of steric hindrance. For example, ions VI and VII, derived from 3-cyclopentylcyclopentene, are sterically hindered and are considered unpolymerizable. Hence, the only reaction that can occur is deprotonation to form alkenes. In the presence of cyclopentene, however, the alkenes formed from ions VI and VII can react further with cyclopentyl carbenium ions to form oligomers via a series of proton elimination/alkylation reactions. In this case, the spiro[4.5]dec-1-ene formed would represent the least hindered alkene and therefore was expected to react further.

Of some interest is a paper by Naro and Dixon,[10] who studied the alumina and sulfuric acid catalyzed dehydration of 6-hydroxyspiro[4.5]decane. Dehydration over alumina at elevated temperature produced approximately equal amounts of alkenes having the decalin and the spiro[4.5]decane ring structures. Dehydration by sulfuric acid, on the other hand, produced mostly the decalin ring. With neither catalyst was the expected bicyclopentyl detected. It would appear that the type of product formed is determined by the kinetic vs. thermodynamic control of the reaction. Other studies on the solvolysis of neopentyl-type tosylates of the spiran series show that a five-membered ring was readily converted to a six-membered ring via ring expansion, while in the case of a six-membered ring, the course of reaction was dependent on the size of the ring bearing the leaving group.[11,12]

The trimers of cyclopentene could result from the addition of cyclopentyl carbenium ions to alkenes derived from ions IV, VI, and VII. This fraction, however, proved to be too complex for detailed analysis, although the predominance of decalin ring structures was evident from the ^{13}C NMR data.[13]

Our observations with cyclopentene in the BF_3 system show that about one-third of the expected reaction occurred and that the major course of reaction at the dimer stage (two-thirds) involved rearrangement. This rearrangement is unique, as the cyclopentylcyclopentenium ion IV undergoes two successive ring expansions to give the decalin ring structure. The formation of decalin rings via ring expansion is not new, but the formation of these from cyclopentene has never been observed prior to the present study. Hence, in any future work with cyclopentene, particularly when cationic catalysts are used, researchers should look for the presence of decalin ring structures among the products of the reaction.

The dimer fraction from cyclohexene oligomerization, by analogy to the cyclopentene oligomerization, was expected to consist of bicyclohexyl and the *cis*- and *trans*-bicyclo[5.5.0]dodecanes. Analysis of this fraction by GLC showed three components in 1, 4, and 95%, respectively, in order of their emergence from the column. When the dimer fraction was spiked with bicyclohexyl, the largest peak in the chromatogram corresponded with the bicyclohexyl peak. The identity of bicyclohexyl was also confirmed by mass spectrometry (MS/GLC)[14] and ^{13}C NMR. Mass spectrometry showed the two minor compounds to be isomeric $C_{12}H_{22}$ (*m/e* 166) but did not reveal their identities. Comparison of the fragmentation patterns of these minor compounds with those of the published spectra for model compounds ruled out the presence of spiro[5.6]dodecane and dimethyldecahydronaphthalene structures.[14] Since the mass spectral data for *cis*- and *trans*-bicyclo[5.5.0]dodecanes were not available, these isomers were prepared by the lithium amide catalyzed isomerization of 1,5,9-cyclododecatriene followed by hydrogenation.[15] Chromatographic analysis showed that bicyclo[5.5.0]dodecanes were not present in the dimer fraction. The most diagnostic clue to the identity of the predominant minor component came from the ^{13}C NMR spectrum, which showed a distinct peak at 15.6 ppm for the methyl group. The compound in question is believed to be 1-methyl-1-cyclohexylcyclopentane, formed via ring contraction of cyclohexyl carbenium ion to 1-methylcyclopentenium ion followed by addition to cyclohexene. Such a possibility was supported by the fact that the recovered cyclohexene contained some methylcyclopentenes.

In a related work, Laber[16] dehydrated 7-hydroxyspiro[5.6]dodecane using zinc chloride and obtained an 80% yield of cyclohexylcyclohexene. In solvolysis studies of the same spiro system, Krapcho and co-workers[11] identified their products, after hydrogenation, as spiro[5.6]dodecane (15%), bicyclohexyl (80%), and an unidentified component (5%). It appears therefore that the formation of two fused seven-membered rings via rings enlargement is energetically unfavorable. In contrast to cyclopentene, the oligomerization of cyclohexene proceeds mostly in the expected manner, but with some rearrangement involving ring contraction (~5%).

The BF_3 oligomerizations require a promoter and an excess of BF_3 over that needed to form a 1:1 molar complex with the promoter. The degree of oligomerization in the BF_3 reaction can be varied by changes in promoter concentration or type and in reaction temperature.[17] The most common promoters include water, alcohols, and carboxylic acids. The unique advantage of many $BF_3{\cdot}HA$ complexes as catalysts apparently lies in the moderate acid strength of the equilibrium $BF_3{\cdot}HA \rightleftharpoons H^+BF_3A^-$.[18] Competing complexation and decomplexation reactions such as $BF_3{\cdot}HA + HA \rightleftharpoons BF_3{\cdot}2HA$ and $BF_3{\cdot}HA \rightleftharpoons BF_3 + HA$ (A = *n*-BuO) explain the necessity of keeping the system saturated with BF_3. Quenching of the reaction mixture with caustic liberates the promoter, which is then washed out with water.

Experimental Section

Both oligomerization and hydrogenation experiments were carried out in a 1-L, 316 stainless steel, magnetically stirred autoclave that was equipped with a stirrer, a heating mantle, and cooling coils (The Autoclave Engineers, Inc.). In a typical experiment, 300 g of cyclopentene (or cyclohexene), 170 g of *n*-hexane, and 3 g of 1-butanol were charged into the autoclave and pressured with BF_3 to 100 psig. The temperature was adjusted to 30–40 °C, the stirring rate was set at 1000 rpm, and the reaction was arbitrarily continued for 1 h, periodically adding BF_3 to maintain a pressure of 100 psig. At the end of the run, the product was discharged into 500 mL of 25% sodium hydroxide solution to give a black, tarlike material, which, when shaken, turned into a bright yellow product. The organic layer was separated and washed 4 times with 400-mL portions of water (final wash was neutral). The product was dried (anhydrous $MgSO_4$), filtered over Celite, and hydrogenated over Ni 0104 catalyst (10 g, 200 °C, 1000 psig of H_2, 1 h). After stripping of cyclopentane and *n*-hexane at atmospheric pressure, the residue (158 g) was distilled via a glass-packed, five theoretical plate, Oldershaw column to give oligomeric fractions. The distribution of oligomers was determined on a Hewlett-Packard 5710A gas chromatograph using an $^1/_8$ in. × 2.5 ft, 5% Dexsil 300 on Chrom W packed column, programed from 90 to 390 °C at 32 °C/min (thermal conductivity detector temperature, 350 °C; injection port temperature, 400 °C; attenuation 1). Detailed composition of isomers was determined with a 0.01 in. × 150 ft poly(phenyl ether) (OS-138) column at 100 °C.

The distribution of oligomers from cyclopentene at 54% cyclopentene conversion was as follows: dimer, 39.2%; trimer, 35.2%; tetramer, 15.3%; pentamer, 10.2%. The dimer fraction, bp 47–55 °C (3.5 mmHg), was found by GLC to consist of *trans*-decalin (22%), bicyclopentyl (33%), and *cis*-decalin (44%), identified by comparison of their retention times to those of authentic standards. ^{13}C NMR (C_6D_6, Me_4Si): *trans*-decalin, δ 27.24 (2, 3, 6, 7), 34.72 (1, 4, 5, 8), 44.22 (9, 10); *cis*-decalin, δ 24.59 (2, 3, 6, 7), 29.77 (1, 4, 5, 8), 36.87 (9, 10); bicyclopentyl, δ 25.80 (3, 4, 3′, 4′), 32.24 (2, 5, 2′, 5′), 46.89 (1, 1′). The integration was in agreement with the GLC data.

Analysis of the hydrogenated trimer fraction (GLC), bp 116–143 °C (0.65 mmHg), showed two major components (16 and 51%, respectively) and eight minor components (33%), ranging in composition from 1 to 9%. The mass spectrum (MS/GLC) showed the major compounds to be isomeric $C_{15}H_{26}$ (*m/e* 206), but no structural information was deduced. The ^{13}C NMR spectrum showed a predominance of decalin ring structures (major peaks at δ 21.96, 25.57, 26.41, 27.78, and 29.02; intermediate peaks at δ 23.97, 36.62, 38.33, 39.55, and 42.65; minor peaks at δ 23.29, 24.60, 29.57, 29.88, 31.05, 32.08, 37.44, 41.89, 45.55, 47.17, and 49.26).

The oligomerization of cyclohexene was carried out under the exact conditions used with cyclopentene. The distribution of oligomers at 74% conversion was as follows: dimer, 44.6%; trimer, 14.5%; tetramer, 35.6%; pentamer, 5.0%.

The hydrogenated dimer fraction, bp 63–68 °C (0.6 mmHg), consisted of bicyclohexyl (95%) and two minor isomers (1 and 4%, respectively). The ^{13}C NMR spectrum was identical with that of authentic bicyclohexyl (δ 27.34 (3, 4, 5, 3′, 4′, 5′), 30.65 (2, 6, 2′, 6′), and 43.88 (1, 1′)) but additionally contained weak peaks at δ 15.60 (CH_3) and δ 21.59, 21.91, 25.90, 33.66, 36.20, 37.70, and 39.52. One of the minor compounds is believed to be 1-methyl-1-cyclohexylcyclopentane.

The hydrogenated trimer fraction, bp 138–156 °C (0.6 mmHg), too complex for detailed analysis, showed three major peaks by GLC (27, 10, and 26%, respectively) and 17 minor peaks, ranging in composition from 1 to 6% each. The ^{13}C NMR spectrum showed an intense peak at δ 27.30, moderate peaks at δ 30.42, 30.72, and 43.85, and weak peaks at δ 21.97, 22.22, 32.30, 34.24, 37.94, 38.55, and 39.75.

Control Experiment. A mixture of 3-cyclopentylcyclopentene (40 g), cyclohexane (250 g), and 1-butanol (0.4 g) was reacted in the autoclave (30 °C, 50 psig of BF_3) for 10 min to trap the initially formed intermediates. On workup as before, followed by distillation, a monomer fraction, bp 40–55 °C (2–3 mmHg), was obtained that contained 1- and 3-cyclopentylcyclopentenes (82%), Δ^{19}-octalin (2%), $\Delta^{9(10)}$-octalin (3%), and spiro[4.5]decenes (13%). After hydrogenation (PtO_2, EtOH, 25 °C, 50 psig of H_2), *cis*-decalin (11%), *trans*-decalin (15%), and spiro[4.5]decane (74%) were detected in the product (bicyclopentyl-free basis), with little oligomers.

Synthesis of Bicyclo[5.5.0]dodecanes. *trans,trans,cis*-1,5,9-Cyclododecatriene (57 g) was added to a solution of the lithium derivative of ethylenediamine (25 g of Li in 530 mL of amine), and the mixture was stirred at 95–100 °C for 1 h. After hydrolysis, extraction with ether, and distillation, 29.9 g of a mixture of bicyclo[5.5.0]dodeca-1,7-diene and bicyclo[5.5.0]dodeca-$\Delta^{1(7)}$-2-diene was obtained: bp 61–63 °C (0.4 mmHg) [lit.[13] bp 97.5–99.5 °C (8 mmHg)]; ^{1}H NMR (CCl_4, Me_4Si) δ 0.7–2.5 (m, 16 H), 5.2–5.9 (m, 2 H).

Hydrogenation of the diene mixture over Ni 0104 (200 °C, 1000 psig of H_2) followed by distillation afforded 13.5 g of bicyclo[5.5.0]dodecane: bp 53–57 °C (0.4 mmHg) [lit.[13] bp 106–107.5 °C (9 mmHg)]; ^{1}H NMR δ 1.1–1.9 (m); GLC, two isomers (14 and 86%); mass spectrum (MS/GLC) of the first isomer (probably trans), *m/e* 166.2 (11%) (M^+), 82.1 (100), 96.2 (83), 67.1 (61), 81.1 (57); mass spectrum of second isomer (cis), *m/e* 166.2 (20%) (M^+), 96.2 (100), 81.1 (97), 82.1 (91), 67.1 (73).

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Monte Carlo Calculation of the Hydrodynamic Radius at the Θ Point. Deviations from Analytical Gaussian Behavior

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I. Introduction

A number of recent papers have been published comparing theoretical[1,2] expressions for the diffusion coefficient for a polymer at infinite dilution with the diffusion coefficient obtained from quasi-elastic light scattering.[3-6]

In a recent comprehensive comparison of theory and experiment, Schmidt and Burchard[3] found that there is a discrepancy between the predicted and theoretical values of the dimensionless parameter ρ_E

$$\rho_E = R_G/R_H \tag{1}$$

where R_G is the z-average radius of gyration of a polymer chain, usually obtained from light scattering or neutron scattering experiments, and R_H is the experimentally obtained mean reciprocal hydrodynamic radius defined[3] in terms of the Stokes law expression

$$1/R_H \equiv \left(\frac{6\pi\eta_0}{kT}\right)D \tag{2}$$

where η_0 is the solvent viscosity, kT the thermal energy, and D the measured z-average translational diffusion coefficient for the polymer obtained from quasi-elastic light scattering. Schmidt and Burchard[3] found ρ_E to be 1.27 ± 0.05 for a large number of experiments on polystyrene in Θ solvents. The above ρ_E deviates from the 1.504 theoretical value of ρ predicted by Kirkwood theory[1] for the analytical Gaussian coil model of the polymer.

These deviations of experiment and theory have yet to be explained, although usually the inadequacies of the Kirkwood dynamical formulation are considered to be the cause of the discrepancy.[2-9]

In this paper, we approach the observed deviation of theory and experiment from a point of view different from what has been proposed before. We compute the diffusion coefficient from the Kirkwood theory with preaveraging for polymer chains at the Θ point by calculating the $1/R$ moment of these chains created by a Monte Carlo simulation in which both excluded volume and nearest-neighbor interaction are included.[10] The value of ρ obtained for such chains is closer to the experimentally obtained ρ and differs from that obtained for an analytical Gaussian coil. The value of ρ obtained from this Monte Carlo calculation, ρ_{MC}, is 1.40 ± 0.01 for chains with an infinite number of monomers.

II. Gaussian Coil Inverse Radius: Slow Approach to Asymptotic Value

In Kirkwood[1] theory, the diffusion constant, D, is given by

$$D = \frac{kT}{N\zeta} + \frac{kT}{6\pi\eta_0}\left\langle\frac{1}{R}\right\rangle \tag{3}$$

where the first term is the free-draining limit, which depends on the friction coefficient (ζ) and the number of statistical segments in the chain (N). Substituting eq 3 in eq 2 yields

$$\frac{1}{R_H} = \left(\frac{3}{\pi}\right)^{1/2}\frac{1}{h^*b'N} + \left\langle\frac{1}{R}\right\rangle \tag{4}$$

where

$$h^* = \frac{\zeta}{(12\pi^3)^{1/2}b'\eta} \tag{5}$$

The value of h^* has been estimated in a variety of ways for various models of the chain. For chain models where b' and N refer to quantities defined in the spring-and-bead model of a polymer chain, Wang[11] considers values of h^* in the range 0.12–0.40.

Because the term involving h^*, the free-draining term, is considered small compared to the $\langle 1/R\rangle$ term for large N, Schmidt and Burchard[3] did not consider it in their estimation of $1/R_H$. For the moment, we, too, shall not consider this term further but rather focus on the calculation of $\langle 1/R\rangle$.

The term $\langle 1/R\rangle$ in Kirkwood theory is defined as

$$\left\langle\frac{1}{R}\right\rangle = \frac{1}{(n+1)^2}\sum_{i\neq j}^{n+1}\left\langle\frac{1}{r_{ij}}\right\rangle \tag{6}$$

where r_{ij} is the distance between beads i and j and n is the number of bonds in the chain. For the analytical Gaussian coil model one has[12]

$$\left\langle\frac{1}{r_{ij}}\right\rangle = \left(\frac{6}{\pi}\right)^{1/2}\left(\frac{1}{|i-j|^{1/2}}\right)\frac{1}{b'} \tag{7}$$

The Gaussian $\langle 1/R\rangle$ was obtained from eq 6 and 7 by replacing the sum by its trapezoid rule integral. The approximate formula

$$\left\langle\frac{1}{R}\right\rangle_G \doteq \left(\frac{6}{\pi}\right)^{1/2}\frac{8}{3b'N^{1/2}}\left[1 - \frac{9}{8N^{1/2}}\right] \tag{8}$$

to order $1/N$ was obtained. Equation 8 gives the term in $1/N^{1/2}$ exactly but gives the coefficient of the $1/N$ only approximately.

Although inexact, the above result shows the slow approach to the asymptotic value of the Gaussian $\langle 1/R\rangle$, $\langle 1/R\rangle_G$, to its limiting value. The mean reciprocal inverse radius has also been computed for values of N to 100 000 using eq 6 and 7 by performing the summation on a com-