Registry No. (Ethylene)·(propylene) (copolymer), 9010-79-1; polyethylene (homopolymer), 9002-88-4; polypropylene (homopolymer, 9003-07-0.

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Quantitative Measurement of Chain Folding in 1,4-*trans*-Polyisoprene Crystals by Carbon-13 NMR Spectroscopy

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ABSTRACT: The amorphous fraction of solution-grown crystals of 1,4-*trans*-polyisoprene (TPI) is considered to be at the surface of the crystals and contains two components, chain folds and noncrystallizing chain ends or cilia. We report the development of an analytical method for the quantitative measurement of the average surface fold and crystal stem lengths in addition to the degree of crystallinity for TPI. This method uses the combination of selective epoxidation of the double bonds in the surface folds and carbon-13 solution NMR measurements. The crystals were suspended in amyl acetate and reacted with *m*-chloroperbenzoic acid at 0 °C until the rate diminished to zero. It was expected that the fold material would react completely and that the crystal stems would not react at all, producing a block copolymer structure. The carbon-13 NMR spectra of the resultant copolymer were analyzed with the aid of TPI and squalene epoxidized in homogeneous solution to several levels of reaction. The NMR data indicate that epoxidation preserves the stereochemistry of the double bonds, producing only the trans oxirane rings. The TPI preparation examined in this study is found to have an average surface fold length of 7.4 monomer units and an average stem length of 4.92 nm. The degree of crystallinity is observed to be 58.9%. The measure of fold length is in good agreement with an earlier estimate based on the lamellar thickness given by electron microscopy for this same TPI sample. The results of this work indicate that the method of nondestructive chemical transformation of the surface folds followed by NMR analysis provides a detailed picture of the morphology of TPI solution-grown crystals.

Introduction

The nature of the noncrystalline material at the surface of polymer crystals has been of interest to polymer scientists for many years.[1,2] Of particular concern are the length of the surface folds and the extent of adjacent reentry. However, most physical methods used to evaluate the amorphous fraction of polymer samples measure the total noncrystalline content and provide little detail as to the nature of the chains in the surface folds. Using a chemical modification technique, Williams et al.[3] found a high degree of adjacent reentry in the chain folding of solution-grown crystals of polyethylene. A similar study[4] using oxidative degradation followed by GPC measurements on melt-crystallized samples of polyethylene indicated the presence of at least some adjacent reentry. Other studies[5] indicate that the crystal surface is rough and that there is some disordered material at the surface. In previous work[6] we combined the technique of epoxidation at the crystal surface with solution NMR analysis to examine in a quantitative fashion the nature of the chain folds in solution-grown crystals of 1,4-*trans*-polybutadiene (TPBD). Values for the average fold length uncorrected for the presence of cilia varied from 3.0 to 5.6 monomer units, suggesting that adjacent reentry predominates. In a subsequent analysis[7] we used solid-state NMR experiments to examine the motion of the surface folds before and after epoxidation of the polymer. We found that the presence of oxirane rings significantly reduces the motion of the fold as compared with that of the unreacted chain fold, although the motion remains more rapid than that of the crystal stems.

In the present work the combination of selective epoxidation of the double bonds in the surface folds followed by solution NMR measurements is developed for the study of the noncrystalline fraction of solution-grown crystals of 1,4-*trans*-polyisoprene (TPI). The amorphous fraction is considered to be at the surface of the crystal and contains two components, chain folds and the noncrystallizing chain ends or cilia. The selective epoxidation of the double bonds in the fold region is accomplished with the use of *m*-chloroperbenzoic acid (MCPBA), a mild, quantitative, but highly selective reagent.

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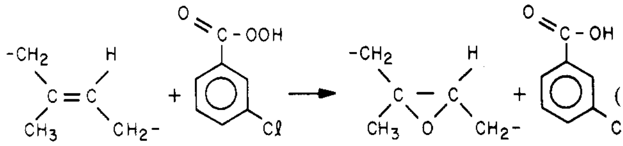

(1)

The reaction preserves the stereochemistry of the double bonds, producing only the trans oxirane rings, as demonstrated previously[6] and again in the present report. The selective epoxidation of the surface folds would result in a block copolymer in which the epoxidized block corresponds to the original chain fold and the diene block is equivalent to the chain stem within the crystal.[8,9] The NMR analysis of the copolymer provides us with a measure of fold length, stem length, and the degree of crystallinity of the polymer sample. The interpretation of the NMR data is materially aided by the study of solution-epoxidized squalene, a structural model for polyisoprene.

We present here the results of our work on TPI. Both this and the previous study on TPBD indicate that the combination of selective chemical modification and NMR analysis provides a quantitative method for examining chain folding in solution-grown polymer crystals.

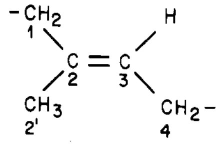
Experimental Section

Sample Preparation. The TPI sample employed in this study is a balata fraction that has been characterized previously.[8] The material was prepared by fractional precipitation from toluene solution with methanol. GPC data indicated a M_n of 290 000 and a M_w/M_n of 1.4. Carbon-13 NMR measurements indicate the trans content to be greater than 99.8%. Crystallization of the polymer from amyl acetate was carried out by dissolution of the material at 80 °C, precipitation at 0 °C, and heating slowly to 40 °C, followed by isothermal crystallization at 20 °C. The crystal suspension was filtered and washed with amyl acetate at 20 °C. Crystals produced by this method are in the α or monoclinic form.[10] The material was then resuspended in amyl acetate for the epoxidation. The density of the dry sample as determined by a water–ethanol density gradient column at 25 °C was 0.975 g/cm^3.

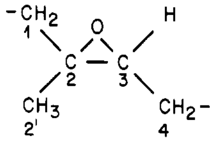
The epoxidation technique involves the addition of MCPBA to the liquid phase of the amyl acetate suspension at 0 °C. The MCPBA is in excess, and the reaction is permitted to proceed until the rate diminishes to zero. Complete details have been given elsewhere.[8] The epoxidized crystals were filtered and dried prior to the carbon-13 NMR measurements. A second sample of the same balata TPI polymer was epoxidized in a homogeneous solution of chloroform to the extent of 25% reaction of the double bonds, reprecipitated from methanol, and dried under vacuum. A third TPI sample, epoxidized to a level of 90%, was also obtained by reaction with MCPBA in chloroform. After the reaction mixture was stirred for 1 h at room temperature it was filtered and washed with 5% sodium bicarbonate solution to extract the *m*-chlorobenzoic acid (MCBA), followed by washing with water and finally with saturated sodium chloride solution. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated on a rotary evaporator at 20 °C. The epoxidized polymer solution was then diluted in chloroform-*d* and concentrated again in vacuo. This particular procedure was found necessary as all attempts to recover and dry the highly epoxidized TPI resulted in an intractable, cross-linked material. Samples of squalene (2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-tetracosahexaene), obtained from Aldrich Chemical Co., were similarly epoxidized to levels of 5, 50, 80, and 100% reaction.

NMR Measurements. The 50.31-MHz carbon-13 NMR spectra of the model squalene and of the polymer samples were recorded at 40 °C on a Varian XL-200 NMR spectrometer. All materials were examined in $CDCl_3$ solutions with concentrations of 40–45% (w/v) for the squalenes and 13–15% for the TPI samples. Hexamethyldisiloxane (HMDS) was used as an internal reference (2.00 ppm vs. Me_4Si). A sweep width of 8000 Hz in 32K of memory with a 90° sampling pulse was employed to collect 150–1000 and 2000–60 000 scans for the squalene and TPI samples, respectively. Pulse repetition times were 5–30 s and broad-band proton decoupling was applied. All quantitative measurements were made by computer integration and in some cases by use of a planimeter as well.

Table I
^{13}C T_1 and NOE Data for 1,4-*trans*-Polyisoprene (TPI) and Epoxidized TPI at 40 °C in $CDCl_3$



carbon	chem shift, ppm	T_1, s	NOE (η + 1)
1	39.85	0.66	2.79
2	134.96	7.79	2.37
2′	16.10	3.80	2.58
3	124.43	1.31	2.79
4	26.88	0.68	2.77



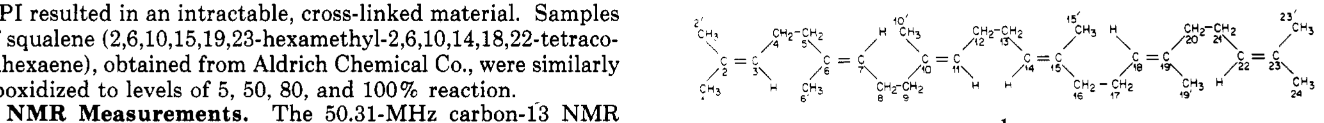
carbon	chem shift, ppm	T_1, s	NOE (η + 1)
1	35.3–35.6	0.44	2.86
2	60.3–60.7	6.3	2.62
2′	16.5–16.8	2.1	2.76
3	62.6–63.3	0.69	2.99
4	24.5–24.7	0.42	2.70

In order to record data in a quantitative manner the appropriate experimental conditions were determined by measurement of the ^{13}C spin-lattice relaxation and the nuclear Overhauser enhancement (NOE). The T_1 measurements were carried out by using a standard 180°–τ–90° inversion–recovery sequence employing a composite 180° pulse,[11] the total delay between 90° sampling pulses being greater than $5T_1$. NOE determinations were made by using the gated decoupling technique, with the delay between each accumulation of data being greater than 10 times T_1 for each carbon nucleus. The results of these measurements are given in Table I.

The 200-MHz ^{1}H NMR spectrum of the epoxidized crystals of TPI was recorded at 40 °C for a 15% (w/v) solution in $CDCl_3$. Only a single transient was necessary to obtain the spectrum. The extent of epoxidation is calculated from both the ^{1}H NMR and ^{13}C NMR data. The results from protonated carbons, only, are used in quantitative determinations made from the carbon NMR data.

Results and Discussion

Carbon-13 NMR Spectra of Squalene Samples. In order to completely interpret the carbon-13 NMR spectra of the epoxidized TPI we have employed squalene as a model for the polymer. The structure of squalene is that of six isoprene units with a tail-to-tail junction in the center. All of the double bonds are in the trans arrangement as in TPI.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Initially discovered as a component of shark liver oil, squalene is now known as a precursor in the biosynthesis of cholesterol, in which the first step is the epoxidation of a terminal double bond.[12]

In Figure 1 spectra for the olefinic and alkyl regions of squalene are shown. In making the assignments for this molecule one need only consider 15 unique carbons owing

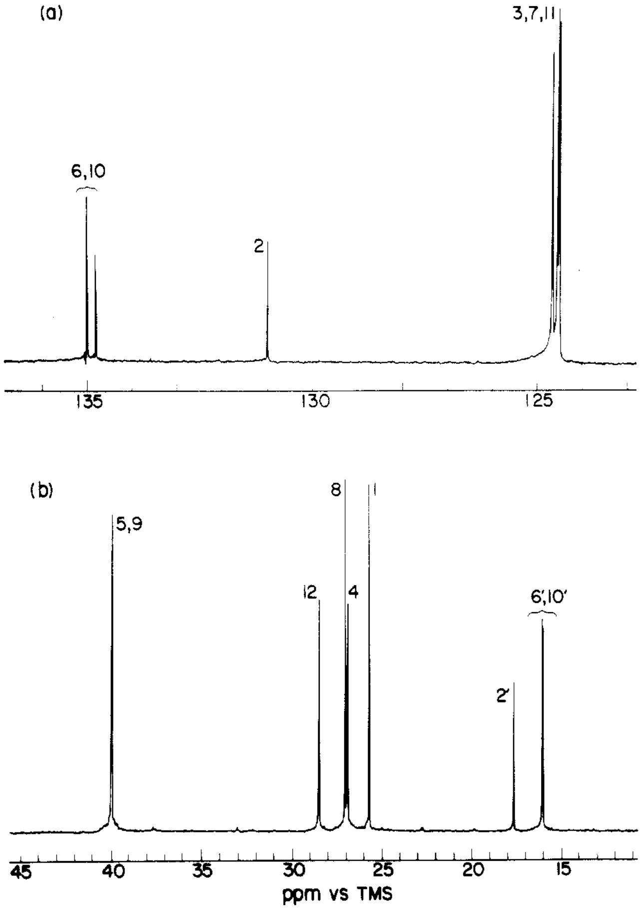
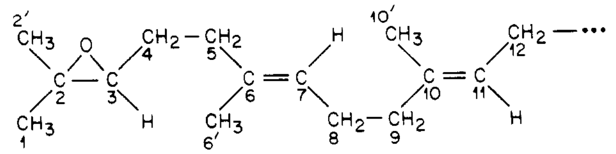


Figure 1. Olefinic (a) and alkyl (b) carbon regions of 50.3-MHz ^{13}C spectrum of squalene. Observed in $CDCl_3$ at 40 °C. Peak designations refer to the carbons of **1**.

to the symmetry about bond 12. A careful examination of the spectrum reveals that at the resonance frequency of 50 MHz the peaks of all 15 carbons can be resolved (peaks 5 and 9 are resolved in an expanded spectrum not shown). The assignments indicated in Figure 1, where peak designations refer to the carbons of 1, are based upon chemical shift prediction rules[13,14] and the results of our DEPT[15,16] experiments carried out on squalene.

Upon epoxidation of squalene in solution the olefinic carbons are converted into oxirane carbons. The spectral region for these nuclei is shown in Figure 2 a–d for squalene epoxidized to levels of 5, 50, 80, and 100%. At the 5% level the oxirane units can be assumed to be isolated by olefinic neighbors. The three possible structural environments generated at this level of epoxidation are as follows:



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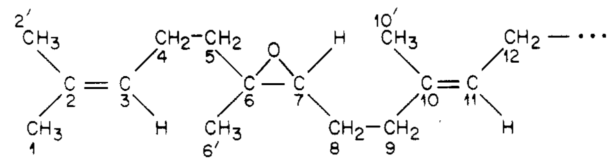

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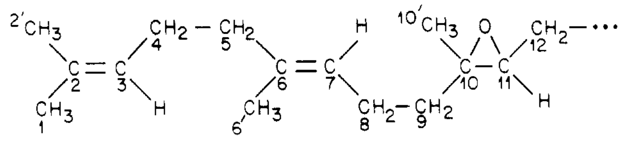

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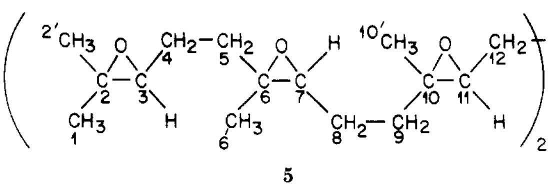
These isolated oxiranes produce the spectrum shown in Figure 2a. The assignments, which refer to the oxirane carbons of **2**, **3**, and **4**, are made on the basis of necessary intensity ratios between internal and terminal units and differences in peak heights for the protonated and nonprotonated carbons. Note that while oxirane carbons 6 and 10 are clearly resolved, oxirane carbons 7 and 11 have identical chemical shifts. The data from this sample clearly show that the isomeric purity of the starting trans olefin is retained following epoxidation. An introduction of cis units would be expected to produce additional resonances in the oxirane carbon region.[16] This point is discussed further in the analysis of the alkyl carbons (see below).

When 50% of the double bonds are epoxidized we find an increase in the complexity of the oxirane carbon spectrum as seen in Figure 2b. In addition to the resonances of isolated oxirane units, we now see peaks generated by changes in the structure of neighboring units. Carbon C2 in the terminal oxirane unit can only sense the presence of one neighbor, olefinic or oxirane. When the neighboring unit is an oxirane we observe that a downfield-shifted pair of resonances is produced. This results from the nonequivalence possible with a pair of oxirane units; i.e., there are two diastereoisomers present. This difference in chirality has been observed earlier in the epoxidation of 3,7-decadiene.[6] The resonance position for the C2 carbon of one diastereoisomer is nearly coincident with that of the C2 carbon in the isolated unit.

Carbon C3 also shows a sensitivity to the chiral relationship between the terminal oxirane and its oxirane neighbor. The resonances of the two diastereoisomers are found one on either side of the resonance for the C3 carbon in the terminal oxirane with an olefinic neighbor. Carbons 6, 7, 10, and 11 may each produce nine individual resonances, considering triad sequences of oxirane and olefinic units and all possible stereosequences. In addition, the tail-to-tail structure about bond 12 of squalene results in a nonequivalence between carbons C7 and C11 when we consider triads of oxirane units. For C7 and C11 we can resolve at least eight resonances, indicating that these internal oxirane carbons, which are excellent models for the TPI, are indeed sensitive to triad stereosequences.

In Figure 2c we see the spectrum of squalene epoxidized to a level of 80%. We see a significant increase in the intensity of the C2 and C3 resonances reflecting the stereochemical isomers relative to intensity of the C2 and C3 resonances of the isolated oxiranes. A loss in the resolution of the C6, -7, -10, and -11 resonances is probably the result of a reduction in the probability of certain olefinic sequences.

The sensitivity of carbon nuclei to different diastereoisomers can be most clearly seen in the spectrum of the 100% epoxidized squalene, **5**, shown in Figure 2d. For both C2 and C3 we observe only the pair of resonances



5

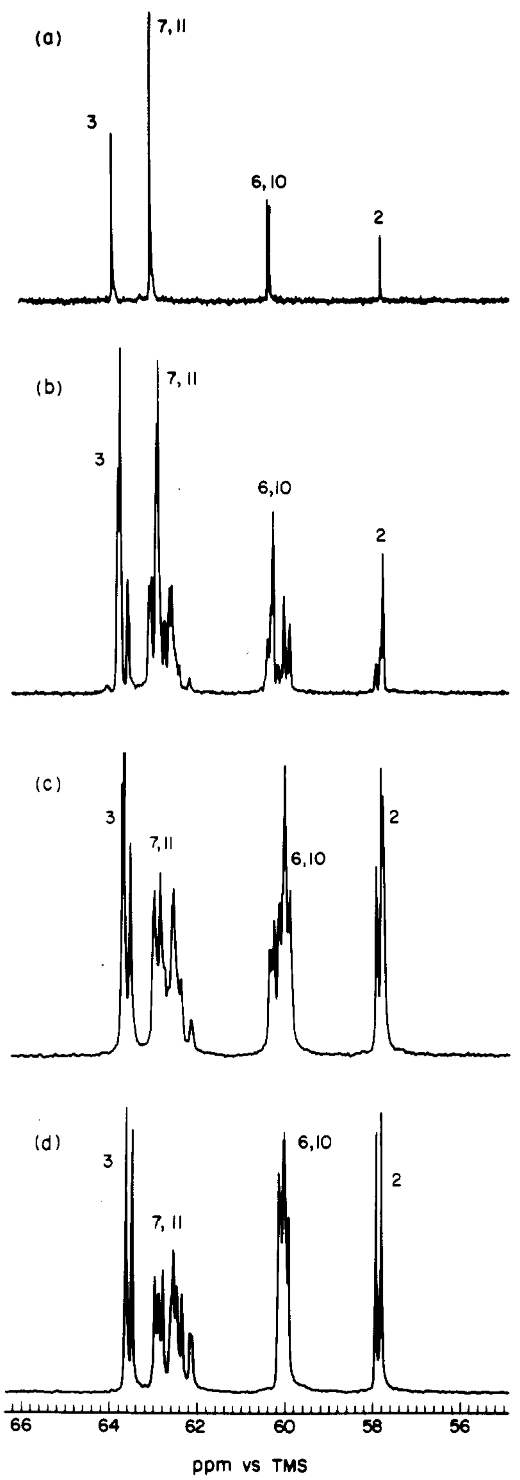


Figure 2. Oxirane carbon region of 50.3-MHz ^{13}C spectra of (a) 5%, (b) 50%, (c) 80%, and (d) 100% epoxidized squalene. Observed in $CDCl_3$ at 40 °C. Peak designations refer to the oxirane carbons of (a) **2**, **3**, **4**, (b) and (c) **2**, **3**, **4**, and **5**, and (d) **5**.

reflecting the two diastereoisomers. This chemical shift separation due to chirality is 0.12 and 0.15 ppm for the C2 and C3 carbons, respectively.

Nonequivalent carbons C7 and C11 of **5** can each generate four resonances reflecting the different stereoisomers, and indeed we see a total of eight peaks at 62.4–63.1 ppm. Similarly C6 and C10 are nonequivalent and might produce eight resonances. The multiplet at 60.0–60.3 ppm contains at least seven lines and represents these nonprotonated carbons.

It should be noted that we observe an upfield shift for some of the resonances, particularly those of carbon C3, as we compare the spectra in Figure 2a–d. In addition, differences in the magnitude of the chiral splitting of resonances can be observed. These small changes in chemical shift may result from longer range structural sensitivity or from changes in the solvent mixture at these high sample concentrations as we move from an olefinic to an oxirane system.

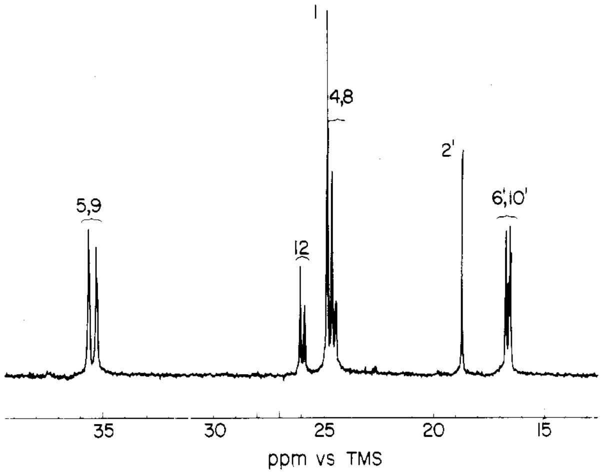


Figure 3. Alkyl carbon region of the 50.3-MHz ^{13}C spectrum of 100% epoxidized squalene. Observed in $CDCl_3$ at 40 °C. Peak designations refer to the carbons of **5**.

The spectral region for the alkyl carbons of **5** is also of interest as a model for our epoxidized TPI. We observe in Figure 3 that the methylene carbons C5 and C9 are shifted upfield by ca. 4.5 ppm relative to their position in **1** (see Figure 1). Methylene carbons C4 and C8 are shifted upfield to a lesser degree, ca. 2.3 ppm. Carbons C5 and C9 display a clear sensitivity to the chirality of the neighboring oxirane units, manifested as a splitting of 0.38 ppm. The magnitude of the splitting for the C4 and C8 carbons is 0.18 ppm, indicating that the methylene carbon attached to the protonated oxirane carbon is less sensitive to the difference between the diastereoisomers. Strong evidence for the preservation of the trans geometry of **1** after complete epoxidation is the absence of a cis C5 or C9 resonance at ~32 ppm, as would be expected based on the ^{13}C spectrum of solution epoxidized *cis*-TPI.[17]

Of the methyl carbons in **5**, C6′ and C10′ most closely model the structure found in a run of oxirane units in epoxidized TPI. The resonances for these carbons have moved downfield ca. 0.6 ppm relative to their position in squalene. The sensitivity of the methyl carbons to the chirality of neighboring oxiranes is demonstrated by the pair of resonances at 16.55 and 16.75 ppm.

From this analysis of the spectra for the oxirane and alkyl carbons in the epoxidized squalenes, we establish two important facts essential in the interpretation of the TPI results, which follows. First, both types of carbons can be expected to show a sensitivity to diastereoisomers with the magnitude of the splitting ranging from 0.12 to 0.38 ppm. Second, the method of epoxidation employed retains the trans geometry of the original olefin.

NMR Spectra of Epoxidized 1,4-*trans*-Polyisoprenes. Figures 4–6 show the carbon-13 spectra for the olefinic, oxiranyl, and alkyl regions of TPI epoxidized in homogeneous solution in chloroform to a level of 25% (spectrum a) and 90% (spectrum b) of completion and epoxidized as crystals suspended in amyl acetate at 0 °C (spectrum c). The assignments and structural formulas are summarized in Tables II–IV, corresponding to Figures 4–6, respectively. The designations shown are based on D for double bond and O for oxirane ring (epoxy unit).

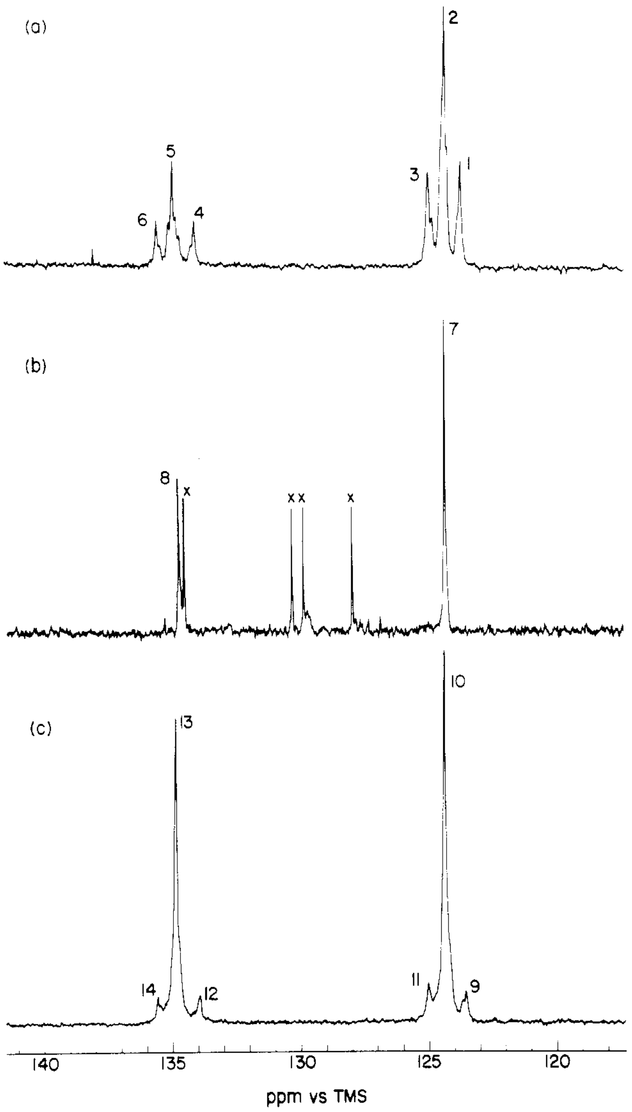
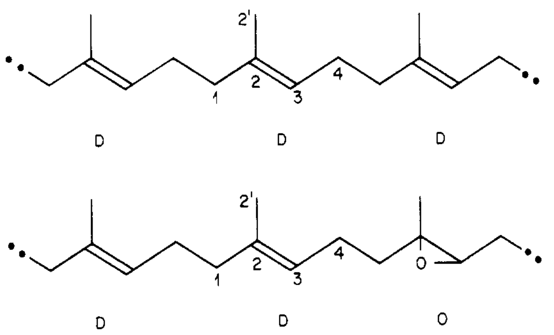


Figure 4. Olefinic carbon region of the 50.3-MHz ^{13}C spectra of (a) 25% and (b) 90% solution-epoxidized and (c) crystal-epoxidized 1,4-*trans*-polyisoprene. Observed in $CDCl_3$ at 40 °C. (See Table II.) ("x", see ref 22.)

The chemical shifts of the polymers are in good agreement with those of the central units in the squalene model discussed above.

In the olefinic region shown in Figure 4 we see the same symmetrical appearance of the spectra as was observed in TPBD.[6] This results from the nonsymmetrical sequences ODD and DDO in which the olefinic carbon is shifted downfield by the presence of an oxirane unit in one direction along the chain and shifted upfield by a similar amount due to the presence of an oxirane unit in the other chain direction. The assignments of resonances 1 and 3 and 4 and 6 are those of Gemmer and Golub, as determined from experiments using lanthanide shift reagents.[17] Fine splittings are observed for some resonances since the olefinic carbons of TPI are sensitive to pentad sequences of O and D units, as was observed for TPBD. As can be seen in the spectrum for the 90% epoxidized TPI (Figure 4b), where the only D-centered sequence is ODO, the presence of oxirane neighbors in both chain directions produces a shift effect much smaller than that observed for a single oxirane neighbor in either chain direction. (Compare ODO vs. ODD or DDO.)

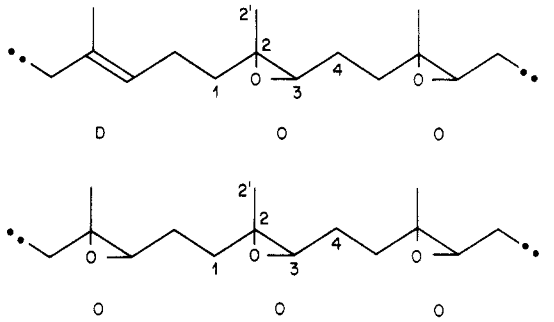
Table II
^{13}C Chemical Shifts of Olefinic Carbons in Epoxidized 1,4-*trans*-Polyisoprene (See Figure 4)[a]



peak desig	assignment	chem shift 25% solution-epoxidized TPI	90% solution-epoxidized TPI	crystal-epoxidized TPI
1, 9	DDO-C3	123.75		123.53
2, 10	DDD-C3	124.43		124.33
3, 11	ODD-C3	125.01		125.00
4, 12	ODD-C2	134.09		133.93
5, 13	DDD-C2	134.95		134.87
6, 14	DDO-C2	135.55		135.58
7	ODO-C3		124.29	
8	ODO-C2		134.72	

[a] Structural formulas of two representative sequences are shown.

Table III
^{13}C Chemical Shifts of Oxirane Ring Carbons in Epoxidized 1,4-*trans*-Polyisoprene (See Figure 5)[a]



peak desig	assignment	chem shift 25% solution-epoxidized TPI	90% solution-epoxidized TPI	crystal-epoxidized TPI
1, 5, 9	OOD-C2 (m,r)	60.22 60.31	60.32 60.44	60.21 60.33
2	DOD-C2	60.69		
2, 6, 10	DOO-C2	60.69	60.70 60.76	60.66
3, 7, 11	DOO-C3	62.94 62.99	62.63–63.31	62.53–63.20
4	DOD-C3	63.09		
4, 8, 12	OOD-C3	63.09	63.31	63.20
5, 9	OOO-C2 (m,r)		60.32 60.44	60.21 60.33
7, 11	OOO-C3 (mm, mr,rm,rr)		62.63 62.82 63.14 63.31	62.53 62.74 63.05 63.20

[a] Structural formulas of two representative sequences are shown.

In the oxirane region shown in Figure 5 we see, as expected, a strong similarity between the spectrum of the 90% solution-epoxidized (5b) and the crystal-epoxidized TPI (5c). In both polymers the oxirane-centered sequences are the OOO, OOD, and DOO. Both oxirane carbons show the sensitivity to chirality observed in epoxidized squalene. For the C2 quaternary carbon the splitting is ca. 0.12 ppm,

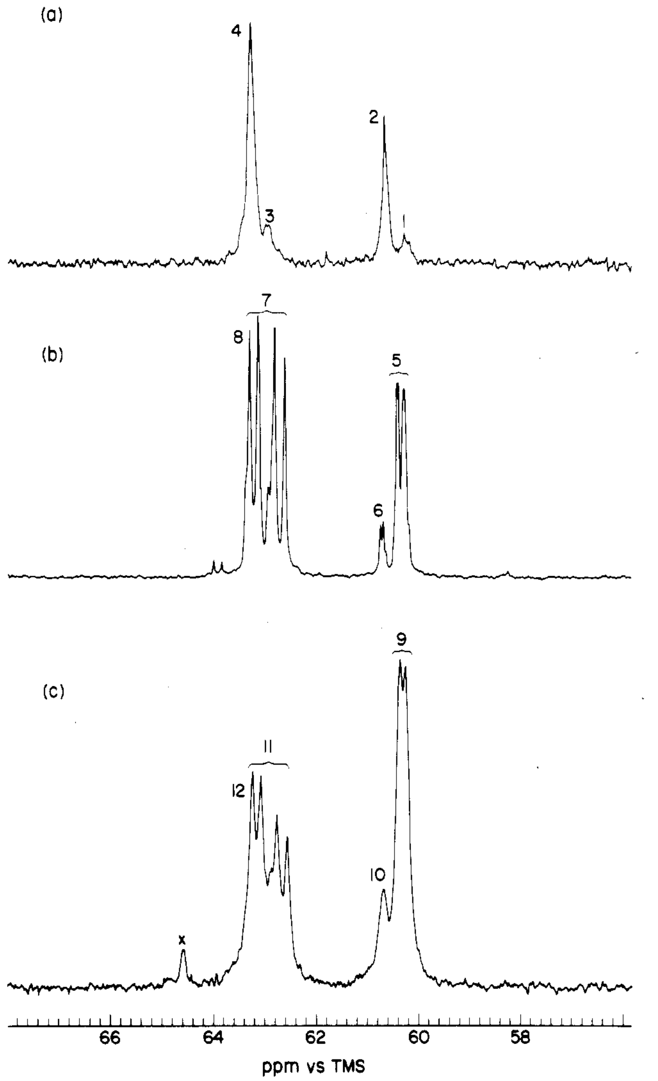


Figure 5. Oxirane carbon region of the 50.3-MHz ^{13}C spectra of (a) 25% and (b) 90% solution-epoxidized and (c) crystal-epoxidized 1,4-*trans*-polyisoprene. Observed at $CDCl_3$ at 40 °C. (See Table III.) ("x" indicates residual amyl acetate.)

reflecting the chiral relationship with only the nearest-neighbor unit. The C3 oxirane carbon is sensitive to the chirality of neighboring units in both directions along the chain and thus is split into a four-line pattern produced by the four possible diastereoisomers,[18] with the spread of shifts equal to ca. 0.68 ppm.

The alkyl carbon region is shown in Figure 6. Comparison of the three spectra permits a consistent set of assignments as given in Table IV. The assignments in spectrum a are in agreement with those made previously on solution-epoxidized TPI.[17,19] However, the original assignment of resonances 10 and 14 was made incorrectly[19] as a result of not considering sensitivity to the diastereoisomers. Resonances 19, 22, 24, and 25 are each a measure of junction units between runs of olefinic and oxirane units and are used analytically in the next section. The small resonances labeled "x" are due to residual amyl acetate used in the epoxidation of the TPI crystals.

Levels of Epoxidation and Degree of Crystallinity. The amount of epoxidation can be established for each sample by a comparison of integrals for the different oxirane and olefinic carbons. The C3 carbons are the most reliable for quantitative analysis based on the relaxation and NOE data of Table I. Using these data we estimate the epoxidation levels to be 25% and 90% for the solution-epoxidized TPI and 41.1% for the crystal-epoxidized TPI. Analysis of a ^{1}H NMR spectrum of the crystal-epoxidized TPI material indicates an extent of epoxidation of 40.4%, in excellent agreement with the ^{13}C NMR results. The amount of amorphous material, 41.1%, as determined by ^{13}C NMR, indicates a level of crystallinity equal to 58.9% for the TPI sample. This compares well with the value of 54% calculated from density measurements.[8]

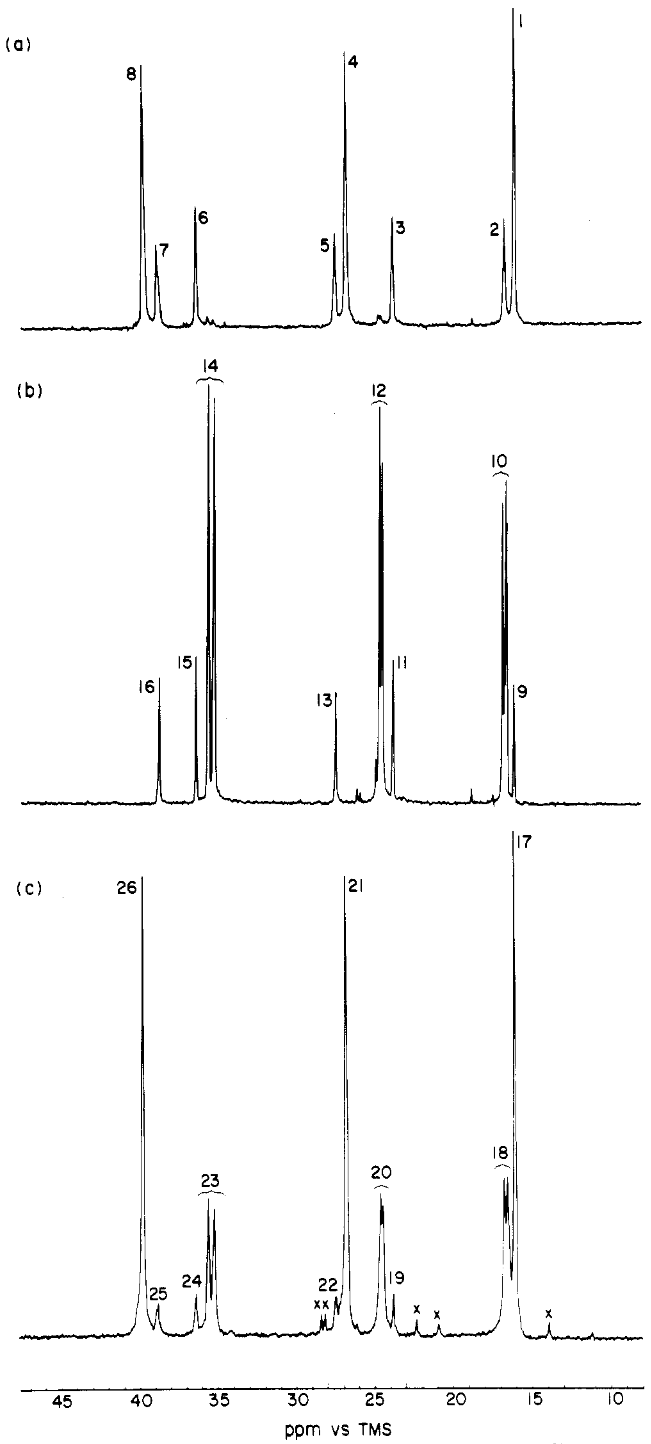
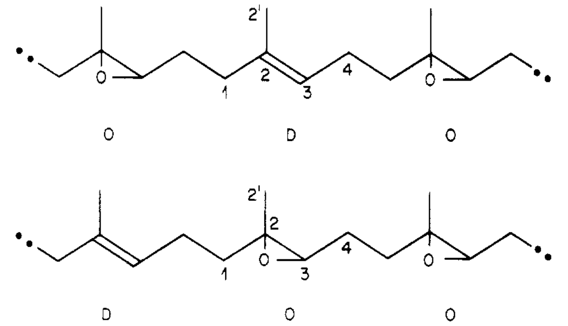


Figure 6. Alkyl carbon region of the 50.3-MHz ^{13}C spectra of (a) 25% and (b) 90% solution-epoxidized and (c) crystal-epoxidized 1,4-*trans*-polyisoprene. Observed in $CDCl_3$ at 40 °C. (See Table IV.) ("x" indicates residual amyl acetate.)

For the crystal epoxidation it is important that we establish complete reaction of the fold material. A complete epoxidation reaction at the surface of the crystals will produce a block copolymer of OOO and DDD sequences with no measurable amount of ODO or DOD sequences. The spectral data of Figure 4–6 provide confirmation of

Table IV
^{13}C Chemical Shifts of Alkyl Carbons in Epoxidized 1,4-*trans*-Polyisoprene (See Figure 6)[a]



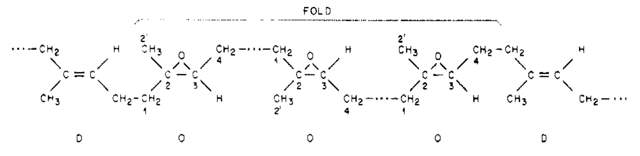
		chem shift		
peak desig	assign-ment	25% solution-epoxidized TPI	90% solution-epoxidized TPI	crystal-epoxidized TPI
1, 17	DDD-C2′	16.10		16.03
	ODD-C2′			
	DDO-C2′			
2	DOD-C2′	16.72		
3, 19	DDO-C4	23.86		23.76
4, 21	DDD-C4	26.88		26.77
	ODD-C4			
5	DOD-C4	27.57		
6, 24	ODD-C1	36.46		36.33
7	DOD-C1	38.98		
8, 26	DDD-C1	39.85		39.75
	DDO-C1			
9	ODO-C2′		16.06	
10, 18	OOD-C2′		16.56	16.47
	DOO-C2′		16.78	16.69
	OOO-C2′			
	(m,r)			
11	ODO-C4		23.80	
12, 20	DOO-C4		24.49	24.42
	OOO-C4		24.66	24.57
	(m,r)			
13, 22	OOD-C4		27.44	27.48
14, 23	OOD-C1		35.24	35.17
	OOO-C1		35.61	35.54
	(m,r)			
15	ODO-C1		36.40	
16, 25	DOO-C1		38.74	38.78

[a] Structural formulas of two representative sequences are shown.

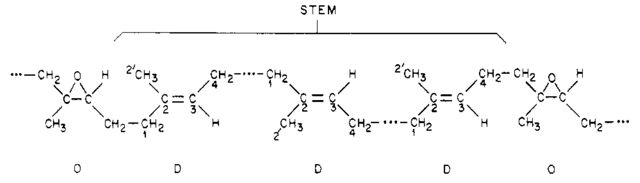
this reaction. An isolated oxirane unit, DOD, can be ruled out by observation of the OOO-C2′ resonances of equal intensity at 16.47 and 16.69 ppm in Figure 6c. The C2′ of residual DOD would produce a single resonance at 16.72 ppm and, therefore, increase the intensity of only one OOO-C2′ resonance.

The presence of the isolated olefinic unit, ODO, can be tested by comparing integrals of ODD-C1 and DOO-C1. The ODO-C1 carbon will add to the intensity of the ODD-C1 resonance but not to that of the DOO-C1 carbon. The observation of equal integrals (within experimental error) confirms the absence of nonepoxidized isoprene units in the folds and demonstrates that the ODD-C1 and DOO-C1 are measurements of the junction between the blocks of oxirane and olefinic units. Therefore, we can conclude that the entire fold region has been epoxidized.

Calculation of Fold Length and Stem Length. Epoxidation of TPI crystals produces an ABABAB block copolymer where A represents the olefinic units in the crystalline stem and B represents the oxirane units of the crystal surface folds. A quantitative comparison of the A block and the B block with the AB junction will yield a measure of the average length in monomer units of the crystal stem and the surface fold, respectively. As a measure of the olefinic A block we can use DDD-C1, -C2, -C3, and -C4 and for the oxirane B block we use OOO-C1, -C2, or -C4. As indicated in **6** and **7** the DOO-C1 and ODD-C1 are measures of the stem–fold junction, as are DDO-C4 and OOD-C4. If $[J]$ is the resonance area of a junction carbon and $[B]$ is the resonance area of a carbon in the oxirane fold, and we let U represent the average fold length in monomer units, then the number of J carbons per fold is 1, the number of B carbons per fold is $U - 1$, and therefore



6



7

$$U = [B]/[J] + 1 \qquad (2)$$

Using eight unique measurements of $[J]$ and $[B]$ from our spectra of epoxidized TPI crystals we find the value of U is 7.0–7.9 monomer units, with the average value of 7.4 monomer units. We do not attempt any correction for chain ends or cilia as this has been shown to be unnecessary for a TPI sample of this molecular weight.[9] This result is in good agreement with a previous estimate of average fold length on this particular TPI sample. With a determination of surface fraction from ^{1}H NMR and lamellar thickness from electron microscopy, a value of U equal to eight monomer units was found, assuming no chain-end correction.[8] In both estimations of average fold length it is assumed that only a minimal amount of dissolution occurs at the sides of the crystal during the epoxidation process.

The stem length, L_s, was determined by a comparison of integrals for olefinic carbons in the A block and for junction carbons as mentioned above. Assuming the repeat distance, R, of an isoprene unit to be 0.439 nm[20] then

$$L_s\ (\text{nm}) = ([A]/[J] + 1)R \qquad (3)$$

where $[A]$ represents the area of a DDD-C1 or -C4 and $[J]$ is that of a junction carbon. The average value found for L_s in this crystalline TPI sample is 11.2 monomer units or 4.92 nm.

For comparison we may also determine the average stem length from the following expression, assuming a large M_n and complete epoxidation of the fold material:

$$L_s\ (\text{nm}) = [(U/f_e) - U]R \qquad (4)$$

The quantity f_e is the fractional extent of epoxidation as determined by carbon-13 NMR (see above). An L_s value of 4.65 nm is found from eq 4.

The crystal thickness, L_c, of the TPI crystals studied has been reported earlier by one of us[8] using electron microscopy measurements of the lamellar thickness, L, and the following relationship:

$$L_c = \frac{(1 - F_s)\rho_a L}{(1 - F_s)\rho_a + F_s\rho_c} \qquad (5)$$

where F_s is the fraction of monomer units at the crystal surface as determined by ^{1}H NMR and ρ_a and ρ_c are the amorphous and crystalline densities, respectively. An L_c value of 4.98 nm is found from eq 5. The crystal thickness can be estimated from our value of the stem length by multiplying L_s and the sine of the angle of inclination for the crystalline stem. If we assume the fold surface is in the 001 plane, the chain tilt will equal the β angle in the unit cell (102°) for the α form.[21] This gives an L_c value of 4.81 nm. However, it should be noted that crystals grown in the manner employed in this work can be curved or cup-shaped, in which case the crystal-growth plane may not be 001.

Conclusions

The method of nondestructive chemical transformation of surface folds followed by high-resolution carbon-13 NMR analysis is demonstrated to be a direct quantitative measure of the surface folds, the crystalline stems, and the fraction crystallinity in solution-grown polymer crystals. This approach should be applicable to other polymer systems in which a suitable chemical treatment can be established.

The values of fold length, U, and stem length, L_s, determined quantitatively from our carbon-13 results for one preparation of TPI crystals, are in excellent agreement with those reported previously based on determinations of surface fraction, crystal and amorphous densities, and the monomer repeat distance.[8] Together these studies present a detailed picture of the morphology of TPI solution-grown crystals.

Results of additional studies on TPI crystalline preparations employing this analytical approach will be presented in a subsequent report. This will include the analysis of the dissolution properties of various suspension liquids employed in the crystal epoxidation of TPI and the effects of crystallization temperature on chain folding. In addition, results of carbon-13 NMR solid-state studies on the α and β forms of TPI will be reported in the near future.

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Registry No. Squalene, 111-02-4.

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(18) In considering a sequence of three oxirane rings in TPI the four diastereoisomers are as follows: R_2R_3–R_2R_3–R_2R_3; R_2R_3–R_2R_3–S_2S_3; S_2S_3–R_2R_3–R_2R_3; S_2S_3–R_2R_3–S_2S_3. The R and S designations represent the chirality of either carbon 2 or carbon 3. Of course, a set of four enantiomers exists in which we interchange all R and S designations in the four sequences above. However, NMR cannot normally distinguish such enantiomers in the absence of a chiral shift reagent or chiral solvent.

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(22) The peaks labeled "x" result from an apparent side reaction in TPI epoxidized to 90% at 20 °C. It is probable that the MCBA is reacting with oxirane to form an ester linkage and a secondary alcohol.

Viscosity of Concentrated Solutions of Rodlike Polymers

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ABSTRACT: Viscosities of aqueous solutions of a triple-helical polysaccharide schizophyllan were measured with four samples of different molecular weights. The data obtained were combined with those reported previously and analyzed theoretically. The seven samples studied consisted of four lower molecular weight samples of rigid-rod shape and three higher molecular weight samples exhibiting flexibility. Zero-shear viscosities η_0 increased with C^5–C^8 in a relatively low range of concentration. There was a maximum in the η_0 vs. C curve for each of the lower molecular weight samples. η_0 at a fixed concentration increased with M^7–M^8 for the rigid-rod samples and approximately with M^5 for the semiflexible samples. For the former samples, the C and M dependence of zero-shear viscosity could be described by Doi's viscosity equation for rodlike polymer solutions when η_0 was replaced by η_e, obtained by subtracting the dilute solution contribution η_d from η_0. Here $\eta_d = \eta_s[1 + C[\eta] + k'(C[\eta])^2]$, where η_s is the solvent viscosity, $[\eta]$ the zero-shear intrinsic viscosity, and k' the Huggins constant. A value of 8.8 was obtained for α, a numerical parameter in the Doi theory. Doi's viscosity equation predicted the absolute value of η_e accurate to 0.03 relative to unity. η_e was much lower for any of the semiflexible samples than for the corresponding rigid rod at a given CM, and the difference varied with the degree of flexibility and polymer concentration. A comparison of the schizophyllan data with those of other rigid polymers showed α not to be universal but characteristic of the polymer–solvent system.

Rodlike polymers disperse randomly in dilute solution, forming an isotropic solution. Above some critical concentration C_A, the solution begins to separate out a liquid crystal phase. The liquid crystal phase increases in volume