model polyethylenes this contribution is significant but probably too small to account for all of the observed behavior. The other is based on differences in the paths for conformational relaxation of linear and branched chains, as suggested in recent theories. Linear chains rearrange by reptation; long branches rearrange by passing through relatively compact conformational states that may have different energies, depending on the temperature coefficient of chain dimensions in the species.

Both mechanisms lead to thermorheological complexity for branched polymer liquids and are able to account for differences in such behavior among polymer species. Both operate in the same direction, and it is not clear how to distinguish them experimentally. We assume that each contributes to the observed behavior.

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Stereochemistry of Poly(1,3-cyclohexadienes). NMR Investigation of Effects due to the Solvent Medium and to the Mechanism of Polymerization

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ABSTRACT: The ^{13}C NMR and ^{1}H NMR spectra of poly(1,3-cyclohexadiene) (PCHD) were analyzed. Anionically polymerized samples, cationically polymerized samples, and samples polymerized with a Ziegler–Natta catalyst were investigated. The ^{1}H NMR and ^{13}C NMR spectra were taken at 270 and 67.88 MHz, respectively. The resolution of the former spectra was incomplete and they were deconvoluted by computer simulation. Relative intensities of the computer-resolved ^{1}H NMR peaks were used in the calculation of the isomeric composition of the investigated PCHD's. ^{1}H NMR results were confirmed qualitatively by ^{13}C NMR results. 3,3′-Bicyclohex-1-enyl (BCH) was used as a model compound for the verification of the proposed assignment of the experimentally observed chemical shifts. The effect of solvents on the microstructure of the anionically polymerized 1,3-cyclohexadiene has been found to be essentially analogous to that observed for the acyclic dienes. Significant differences were, however, detected. For example, even in polar solvents the fraction of 1,2 isomers did not exceed 50%. Apparently, steric hindrance precludes the formation of long sequences of 1,2 units. The formation of intermittent 1,2 and 1,4 sequences is feasible and their fraction increases with increasing temperature. The anionic polymerization of 1,3-cyclohexadiene in hexane and in bulk yields the 1,4 isomer in a predominantly cis-type planomeric conformation. The stereoselectivity of the cationic and the Ziegler–Natta systems is lower than that of the anionic ones.

Introduction

Polymers and copolymers of acyclic dienes have been thoroughly investigated, and the effect of the conditions of polymerization on their structural features has been elucidated.[1] Much less is known about polymers of their cyclic analogue 1,3-cyclohexadiene (CHD).

Several applications of poly(cyclohexadienes) (PCHD) were proposed, and knowledge of their microstructure is of considerable interest. It has been shown, for example, that the copolymer of CHD and pentadiene acts as an active ingredient of photomicrolithographic screens, and the optical resolution of such devices is greatly enhanced

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by addition of PCHD.[2] Doping of poly(*p*-phenylenes) with AsF_6 yields highly conductive polymers.[3] It has been demonstrated[4,5] that the dehydrogenation of PCHD yields polyphenylenic segments. It was also suggested[6] that the high hydrolytic stability of PCHD may make them useful as undersea plastic materials.

The polymerization of CHD may be initiated by free radical, Ziegler–Natta, or transition-metal-type catalysts[4-8] as well as by cationic or anionic initiators.[4-6,9-11] One may expect that the structure of PCHD's may be strongly affected by the polymerization mechanism and by the solvent medium. Solvent effects in the anionic polymerization of the acyclic dienes[1,12-14] were extensively investigated. It was found that polar solvents promote the 1,2 mode of addition. It was also found that the 1,4-cis isomers are formed in apolar noncomplexing solvents when lithium alkyls are used as initiators. The cyclic structure of CHD determines a priori the cis configuration of the carbons adjacent to the double bonds in PCHD. Cis or trans conformers with respect to the plane of the rings may, however, be envisaged. The term planomers has been coined to describe such configurational isomers.

Lefebvre and Dowans,[5] who were the first to polymerize CHD with alkyllithium, claimed that the 1,2 and 1,4 isomers of PCHD are formed in polar and apolar solvents, respectively. They did not substantiate, however, their claims by strong experimental evidence. Review of subsequent literature on the subject reveals a fragmentary and rather confusing picture. Naumova et al.[9] came to the conclusion that only 1,4-PCHD's are formed in polymerizations initiated by BuLi in THF as well as in bulk. 1,4-PCHD was also claimed to be the sole product of the polymerization of CHD initiated by the allyl chloride–nickel complex.[8] On the other hand, Lenz and Mango claimed[6] that the 1,2 and not the 1,4 mode of addition is dominant in polymerizations of CHD in apolar as well as polar solvents.

Recently, the mechanism and the kinetics of the anionic polymerization of CHD were investigated in this laboratory.[11] We decided to use high-field NMR spectroscopy for elucidation of the structural features of such polymers and of PCHD's obtained by other polymerization techniques. ^{13}C NMR spectra at 67.88 MHz and ^1H NMR spectra of PCHD's at 270 MHz were recorded and their interpretation is discussed in the present paper.

Experimental Section

Preparation of PCHD samples was described elsewhere.[11,15] 3,3′-Bicyclohex-1-enyl (~98% purity) was synthesized in our laboratory via Grignard coupling of 3-chlorocyclohexene. The ^1H NMR and natural-abundance, ^1H-decoupled, ^{13}C NMR measurements were performed on a WH 270 Bruker instrument with Fourier transform. The 270- and 67.88-MHz frequency modes were used in the ^1H and ^{13}C NMR measurements, respectively. Deuterated chloroform (99.8% isotopic purity, Merck Sharp and Dohme) was used as a solvent, with peaks referred to $\delta(Me_4Si) = 0.00$. Standard NMR tubes (Wilmard) were used in all experiments. Further resolution of the resonance signals in the recorded ^1H NMR spectra was attained by a computer simulation procedure. The ω_i and A_i coordinates of the experimental NMR curves were digitized with a D-MAC digitizer. Computer resolution was carried out assuming a Lorentzian shape of the resonance peaks.

The computer iteration procedure utilized a general optimization package with algorithms for minimizing the sum of the squares, using the LMCHOL routine, which is a modularized modification of the computer algorithm VAOZA (R. Fletcher, Harwell report R.6799). The curve fit was adjusted by minimizing the discrepancy defined as $\{\sum A^2/n\}^{1/2}$, where A is the difference between the calculated and the experimental points and n is the number of points considered.

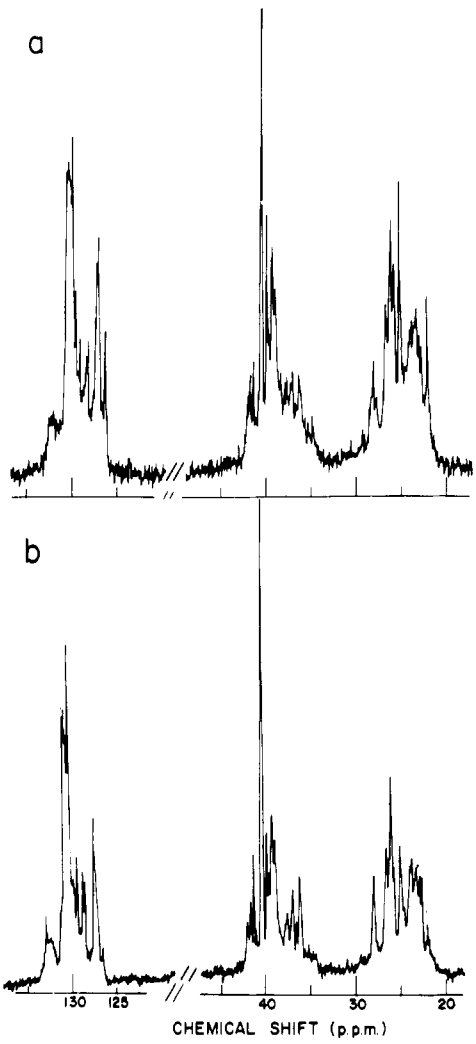


Figure 1. 67.88-MHz proton-decoupled ^{13}C NMR spectra of PCHD's polymerized anionically in THF at −20 °C ($CDCl_3$, referred to Me_4Si): (a) lithium naphthalenide (N^-,Li^+) as initiator; (b) butyllithium (BuLi) as initiator.

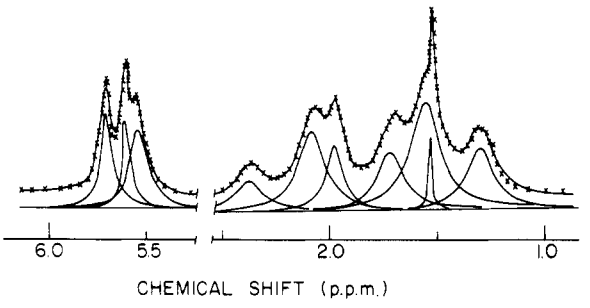


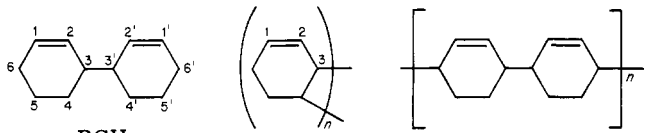
Figure 2. Computer-resolved ^1H NMR spectrum of PCHD polymerized anionically in THF at −20 °C with N^-,Li^+ as initiator. X's denote the digitized points taken from the original spectrum. Full lines represent the computer-simulated spectrum and the computer-resolved signals.

Results and Discussion

^{13}C NMR spectra of the PCHD's formed in THF at −20 °C in the presence of lithium naphthalenide (N^-,Li^+) and of butyllithium (BuLi) as initiators are shown in Figure 1a,b, respectively. The two spectra, which are very similar, cannot unambiguously be attributed to only 1,4-PCHD. The ^1H NMR of the first sample is shown in Figure 2. Ten peaks are obtained by computer resolution of the recorded spectrum (cf. full lines in Figure 2). The peaks at ca. 1.50, 1.98, and 5.75 ppm, which were ascribed[8,9] to

crystalline 1,4-PCHD, and the peak at ca. 5.57 ppm, which was ascribed to the olefinic protons of amorphous 1,4-PCHD, are, indeed, detected in the resolved spectrum. Several additional resonance lines are, however, also present. Obviously, the structure of the polymer formed is more complicated than that expected for pure 1,4-PCHD or pure 1,2-PCHD (numbers before PCHD indicate the mode of addition of CHD and do not correspond to the numbering of substituents in cyclohexene rings formed during polymerization). A model compound was analyzed to obtain additional information required for the assignment of the resonance lines.

^{1}H NMR and ^{13}C NMR Spectra of 3,3′-Bicyclohex-1-enyl (BCH). Exact models of various isomeric forms



BCH 1,2-PCHD 1,4-PCHD

of PCHD would be provided by trimers derived by substitution of cyclohexene in positions 3 and 6 or 3 and 4, respectively, with cyclohexenyls. However, such trimers were not available and we decided to use BCH as the model compound. The chemical shifts of carbons 1, 2, and 6 and of their protons should be close to those of 1,2-PCHD if they are not affected significantly by a substituent in the β position (on C_4). The chemical shifts of carbons 2, 3, and 4 and of their protons should closely resemble those of the 1,4-PCHD. Approximations involved in such assumptions seem to be reasonable in view of the known effects of substituents on ^{13}C and ^{1}H chemical shifts of cyclohexene;[16] e.g., the vinyl protons of 3,4-dimethylcyclohexene were reported[6] to be characterized by a multiplet at 5.43–5.55 ppm, while those of 3-cyclohexene[15] were characterized by an ABX pattern at 5.50–5.64 ppm.

The ^{13}C NMR spectrum of BCH, shown in Figure 3a, has eleven resonance lines instead of the expected six (the magnetic environments of carbons in the two rings should not differ). This suggests that two isomeric forms are detected by ^{13}C NMR. The two rings connected at carbons C_3 and $C_{3'}$ may be located as (1) eq′/eq′, (2) eq′/ax′, or (3) ax′/ax′ (primes are used to indicate the pseudoequatorial and the pseudoaxial character of those bonds in cyclohexene[17]). Thus, three planomeric conformers of BCH should exist. They could be detected by NMR if the inversion of the cyclohexene rings is slow on the NMR scale. Unsubstituted cyclohexene ring inversion is, however, fast, and substitution by a cyclohexenyl ring should not slow it down significantly. Inspection of the ^{1}H NMR spectrum of BCH, shown in Figure 3b, also indicates a fast inversion; i.e., a single broad peak at 2.12 ppm, due to H_3, is observed. It must be regarded as an average of its pseudoequatorial and pseudoaxial chemical shifts. On the other hand, the three multiplets (at 1.72, 1.51, and 1.35 ppm) of the β-methylene protons must be attributed to the nonequivalency of the geminal protons at C_4 and at C_5 due to the asymmetric center at C_3. Though the inversion of a single cyclohexene ring of BCH seems to be fast, the simultaneous inversion of its two rings, required for transition from the conformer eq′/eq′ to the conformer ax′/ax′, may be slow on the NMR scale. The two sets of resonance lines observed in the ^{13}C NMR spectrum of BCH may therefore correspond to mixtures of eq′/eq′ + eq′/ax′ planomers and ax′/ax′ + ax′/eq′ planomers. Alternatively, they may be ascribed to magnetic nonequivalence of the threo and erythro enantiomers of BCH. The proposed assignment of the resonance lines of the BCH planomers to specific

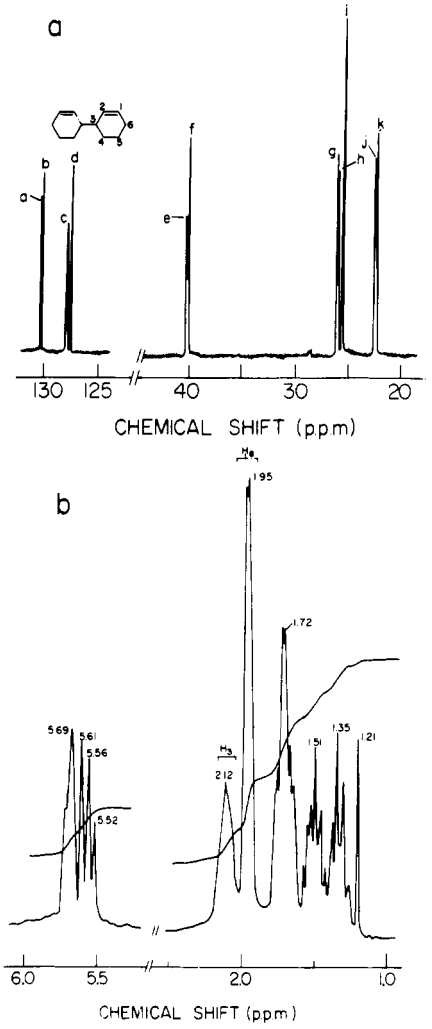


Figure 3. NMR spectra of 3,3′-bicyclohex-1-enyl (BCH) ($CDCl_3$, referred to Me_4Si): (a) 67.88-MHz proton-decoupled ^{13}C NMR spectrum; (b) 270-MHz ^{1}H NMR spectrum.

carbons and protons is summarized in Table I. The reported[16,17] chemical shifts of cyclohexene and PCHD are also listed for the sake of comparison.

Calculation of the Isomeric Composition of PCHD. 1,4-PCHD, 1,2-PCHD, and polymers comprising both the 1,4 and the 1,2 units will be formed according to the mode of addition of CHD to the growing chains. Each polymer may exist in geometrically isomeric forms corresponding to different modes of insertion with respect to the cyclohexene ring planes. Only differences in tacticity and in cis or trans placement with respect to the planes of individual rings will be detected by NMR if the inversion of the cyclohexene rings is fast. Tacticity is defined with respect to the plane formed by the chain-forming carbon atoms. Such an alignment of carbon atoms is fictitious for chains consisting of cyclohexene rings in the half-chair form, which is the predominant form for monomeric cyclohexene.[17] A nearly planar alignment of long sequences of PCHD would, however, be possible if the cyclohexene rings are in the half-boat form. For certain conformations of PCHD the requirement for a minimum in repulsion and a maximum in entropy may lead to such forms.

General considerations regarding the expected features of the NMR spectra of PCHD together with the experimentally determined chemical shifts of BCH permit formulation of certain guidelines for the determination by NMR of the structural and geometric isomerism of PCHD. Signals at ca. 25.5 and 127–128 ppm, characteristic of the ^{13}C NMR chemical shifts of the unsubstituted α-CH_2 of

Table I. Chemical Shifts of BCH and Cyclohexene in Chloroform (ppm)

compound	planomer	1		2		3		6		4		5		remarks
		^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	
cyclohexene		5.59	127.2	5.59	127.2	1.96	25.5	1.96	25.5	1.65	23.1	1.65	23.1	ref 16, 17
BCH (3,3′-bicyclohex-1-enyl)	ax′/ax′	5.54	127.71	5.69	130.52	2.12	40.2	1.95	25.5	H_A = 1.51	26.14	H_A = 1.35	22.31	
	ax′/eq′									H_B = 1.72		H_B = 1.72		J_{12} = 10.8 Hz
	eq′/eq′	5.59	128.05	5.71	130.72	2.12	40.3	1.95	25.5	H_A = 1.51	26.07	H_A = 1.35	22.38	(0.04 ppm at 270 MHz)
	eq′/ax′									H_B = 1.72		H_B = 1.72		
crystalline oligomer (1,4-PCHD)		5.75		5.75		1.98		1.98		1.50		1.50		ref 8
amorphous oligomer		5.57		5.57		1.95		1.95		1.50		1.50		ref 8
oligomer (1,4-PCHD)?	cis	5.58		5.58		1.99		1.99		1.54		1.54		ref 9

Table II. Relative Integrated Intensities of the Computer-Resolved ^1H NMR Peaks

			chemical shift,[a] ppm																
			olefinic protons				methylene protons				β protons								
no.	conditions of polymerization	DP	5.71	5.62	5.55	ΣH_{ol}	2.37, 2.17	2.07	1.98	ΣH_α	1.75 ± 0.03	1.60	1.55	1.32	ΣH_β	ΣH	r^c	R^d	$H_{1.75}/H_{2.37}$
1	−20 °C, THF, $N^{-}\cdot,Li^+$	300	0.7	0.5	0.8	2.0	0.5	1.25	0.65	2.40	1.0	1.9	0.2	1.0	4.1	8.5	3.25	1.71	4.0
2	−20 °C, DME, $N^{-}\cdot,Na^+$	230	0.8	0.56	0.64	2.0	0.46	1.42	0.42	2.3	1.04		2.08	1.04	4.16	8.45	3.23	1.80	4.5
3	+25 °C, DME, $N^{-}\cdot,Na^+$	95	0.8	0.46	0.54	2.0	0.36	1.74	0.78	2.88	1.42		2.30	1.02	4.74	9.62	3.81	1.64	?
4	+25 °C, THF, $N^{-}\cdot,Na^+$	55	0.65	0.88	0.47	2.0	0.33	1.78	0.73	2.85	1.24		2.73	0.89	4.86	9.71	3.85	1.71	?
5	+25 °C, hexane, BuLi	9	1.25	0.75		2.0	0.25	1.20		1.45	0.6		2.0	0.5	3.10	6.55	2.27	2.14	4.4
6	+25 °C, heptane, 1/1 $AlEt_3/TiCl_4$	75	1.05	0.95		2.0	0.31	3.13		3.44	1.63		6.12	3.31	11.06	16.5	7.25	3.21	?
7	+10 °C, in bulk, K + $N^{-}\cdot,K^+$	50	0.98	1.02		2.0	0.20	1.81		2.01	0.54	2.95		0.50	3.99	8.0	3.0	1.98	4.4
8	25 °C, benzene, $AlCl_3$		0.64[b] 1.36			2.0	0.05	1.25		1.30	0.25	1.04	5.33	0.26	6.88	10.18	4.09	5.29	5.0

[a] Actual observed values may differ by ±0.01 to ±0.03 ppm from the listed chemical shifts. [b] At 5.78 ppm. [c] $r = (\Sigma H_\beta + \Sigma H_\alpha)/\Sigma H_{ol}$. [d] $\Sigma H_\beta/\Sigma H_\alpha$.

Table III. Isomeric Composition of PCHD's Calculated from Data Listed in Table II

				1,4-CHD, %			cis planomers, %				
no.	conditions of the polymerization	DP	f_H	$f_{1,4}$[a] from eq 2	$f_{1,4}$ from eq 3a	av	f_{cis} from eq 4	f_{cis} from eq 5	*cis*-1,4-PCHD,[b] %	*trans*-1,4-PCHD, %	*trans*-1,2-PCHD,[b] %
1	$N^{-}\cdot,Li^+$, −20 °C, THF	300	0.04 (0.02)[c]	63–71	68	67	46	46–48	47	20	33
2	$N^{-}\cdot,Na^+$, −20 °C, DME	230	0.004	70	79	75	50	44	47	28	25
3	$N^{-}\cdot,Na^+$, +25 °C, DME	95	0.14?	(53)	62	57	48	?	48	9	43
4	$N^{-}\cdot,Na^+$, +25 °C, THF	50	0.145?	(57)	65	61	55	?	55	6	39
5	BuLi, +25 °C, hexane	9	0?	~(100)	100	~100	65	65	65	~34	~1[d]
6	$AlEt_3/TiCl_4$, +25 °C, heptane	75	0.46?	?	100?		55	50	52	~38	~10[d]
7	K + $N^{-}\cdot,K^+$, +10 °C, in bulk	50	0.0	(98)	100	99	74		74	25	1

[a] Values in parentheses were calculated from eq 1. [b] 1,2 cis was assumed to be nil. [c] Calculated from the relationship $f_H = 0.8(H_{1.56}/\Sigma H)$ on the assumption that the resolved peaks at 1.55 and 1.60 ppm correspond to protons of the reduced rings and of the cyclohexene cis β-protons, respectively. All other values were calculated from $\Sigma H_{ol}/\Sigma H_a$ (see text). [d] Estimated from the intensity of the ^{13}C NMR signals in the 127–128-ppm region.

cyclohexene and of the adjacent vinyl, respectively, identify unequivocally the 1,2 units of PCHD. Quantitative calculations based on proton-decoupled ^{13}C NMR are, however, unreliable. The ^1H NMR chemical shifts of the olefinic protons of PCHD should also be different for the 1,2 and 1,4 adducts (an AB pattern is expected for the former and a singlet for the cis planomers of the latter). The effect of the neighboring units and differences in tacticity seem, however, to complicate the picture and make the analysis based on the intensities of the olefinic signals difficult. It was suggested[6,8] that the ratio between the 1,4 and 1,2 fractions of PCHD may be determined by comparing the relative intensities of signals due to α- and β-methylene protons, since H_β/H_α is equal to 2 for 1,4-PCHD segments and 1 for 1,2-PCHD segments. Hence

$$f_{1,4} = (3R - 3)/(R + 1) \quad (1)$$

where $f_{1,4}$ is the fraction of 1,4 added units (3,6-substituted cyclohexene) and $R = H_\beta/H_\alpha$.

Derivation of eq 1 is based on the implicit assumption that an analyzed sample of PCHD consists solely of cyclohexene rings. Thus, calculated values will be incorrect if cyclohexane and cyclohexadiene rings are also present. Chain transfer and termination[6,11] reactions may, indeed, lead to hydrogenation and to dehydrogenation of the cyclohexene rings. The fraction of hydrogenated rings, f_H, in the PCHD samples may be estimated by comparing the intensities of the ^1H NMR signals due to aliphatic (H_a) and olefinic (H_{ol}) protons, respectively, $r = H_a/H_{ol}$. Different modes of addition to the double bond and the presence of dehydrogenated rings will, however, complicate the calculation. Let us assume that the fraction of the latter rings is negligible (this assumption is justifiable for PCHD's obtained by anionic polymerization at low temperature[11]). The value of f_H may then be calculated from the relationship $f_H = (r - 3)/(r + 2)$ or $f_H = (r - 3)/(r + 1)$, the former equation being valid when the disappearance of the double bonds is due to protonation and the latter when it is due to branching or cyclization. Correction for the presence of a fraction of hydrogenated rings yields (in the absence of dehydrogenation) the expression

$$f_{1,4} = [3R - (3 + 7f_H)/(1 - f_H)]/(R + 1) \quad (2)$$

The value of $f_{1,4}$ yields the value of $f_{1,2}$, since $f_{1,4} + f_{1,2} = 1$. An independent direct determination of $f_{1,2}$ is also possible, since the peak at 1.95–1.98 ppm, characteristic of the unsubstituted α-CH_2, identifies uniquely the 1,2 segments. Thus

$$f_{1,2} = 4r_{1.98} \quad (3)$$

$$f_{1,4} = 1 - 4r_{1.98} \quad (3a)$$

where $r_{1.98} = H_{1.98}/(\sum H - 10f_H)$. (For normalized peak intensities the correction due to protons of the hydrogenated rings is given by $10f_H$.)

Let us now consider the geometric isomerism of PCHD. We suggest that for the 1,2 adduct, the cis-type insertion may be, a priori, ruled out on entropy grounds. Molecular models reveal that the freedom of rotation of the cyclohexene rings in the chain would be severely restricted by repulsive forces if two rings attached to vicinal carbons were located on the same side of the cyclohexene ring. Such steric restrictions do not apply, however, to the 1,4 adducts.

Differences between the ^1H NMR spectra of the cis and trans planomers of PCHD are expected for symmetry reasons. Effects due to the two asymmetric centers at C_3 and C_6 must be felt in the trans planomer but not in the cis planomer, since the cis placement creates a new plane

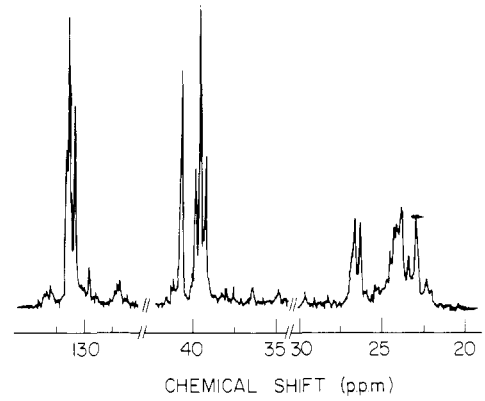


Figure 4. 67.88-MHz proton-decoupled ^{13}C NMR spectrum of the PCHD obtained in hexane with BuLi as initiator ($CDCl_3$, referred to Me_4Si).

of symmetry. Thus, in the trans planomer the nonequivalency of the geminal protons at C_4 and C_5 should be manifested by their ABX patterns. In the spectra of the trans polymers two broad peaks may, therefore, be expected. Their chemical shifts should be close to those of the H_5 protons of BCH. Hence, peaks at ca. 1.35 and 1.75 ppm are expected for the trans planomers and a single peak at ca. 1.6 ppm is expected for the cis-1,4 planomer. The 1,2-trans PCHD may have a somewhat more complicated spectrum, but a clear-cut distinction between the signals of the β protons of the two polymers is not possible. Lenz and Mango[6] observed differences between the ^1H NMR spectra of *cis*- and *trans*-poly(cyclohexanes). These investigators did not observe, however, such differences for PCHD, because of the poor resolution of the 60-MHz ^1H NMR spectra recorded by them.

Comparison of the area of the central peak H_C at ~1.6 ppm with the integrated area of peaks due to all β protons yields the fraction of cis planomers.

$$f_{cis} = H_C/\sum H_\beta \quad (4)$$

$$f_{cis}^{corr} = (H_C - 10f_H + H_{1.35} - H_{1.75})/(\sum H_\beta - 10f_H) \quad (5)$$

Peak intensities must be normalized before being introduced into eq 5. The overall intensity of the olefinic protons is used as a reference. We assigned to it the value of 2.

Analysis of the Spectra of the Investigated Samples of PCHD. The ^{13}C NMR and ^1H NMR spectra of the PCHD's formed in THF with $N^-\cdot,Li^+$ and BuLi initiators were shown in Figures 1 and 2. A much simpler spectrum, however, is obtained when hexane is used as a solvent and will be used as a starting point for this discussion. Inspection of the ^{13}C NMR spectrum shown in Figure 4 reveals a barely detectable signal at 127.5 ppm and no resonance at all at 25.5 ppm. Obviously, 1,4-PCHD is the main product formed under such conditions. This conclusion is confirmed by the ^1H NMR spectrum in Figure 5. Inspection of the spectrum shown in Figure 5 also indicates that the main fraction of this PCHD is in the cis-planomeric form, since the central peak at 1.60 is the dominant one, while peaks at 1.35 and 1.75 ppm appear as small side bands. These qualitative conclusions are confirmed by quantitative calculations. The integrated intensities of the computer-resolved resonance signals of PCHD samples polymerized under various conditions are summarized in Table II. The tabulated values are used to solve eq 1–5. The calculated isomeric compositions of the investigated samples are listed in Table III. Please note the agreement between values of $f_{1,4}$ calculated from

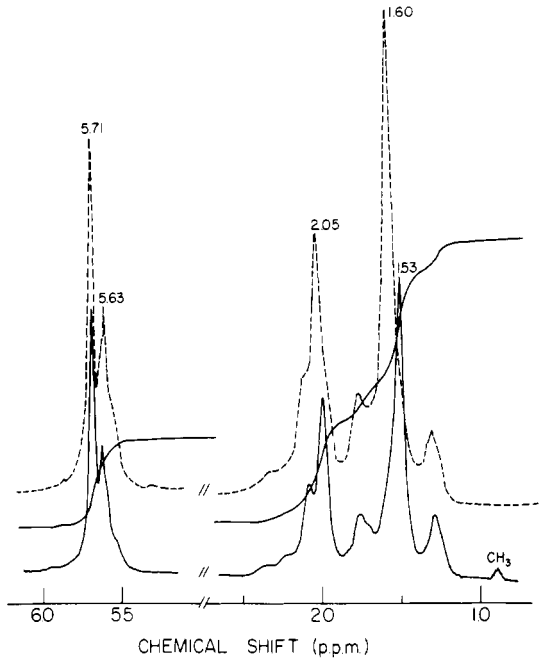


Figure 5. 270-MHz ^1H NMR spectra of PCHD samples ($CDCl_3$, referred to Me_4Si): full line, in hexane, BuLi as initiator; dashed line, in bulk. Removal of the solvent from N^-,K^+ under high vacuum yielded potassium as initiator.

eq 2 and 3a, respectively, when the fraction of hydrogenated rings is small.

Equation 2 could not be applied for PCHD polymerized anionically at room temperature, a reaction accompanied by considerable dehydrogenation.[11] However, for these samples, values derived from eq 1 were in reasonable agreement with those derived from eq 3 and with estimates based on their ^{13}C NMR. Apparently, the additional terms due to hydrogenated and dehydrogenated rings more or less cancel in these samples.

Inspection of the tabulated results reveals similarities between the observed effects and those reported in the literature for butadiene and isoprene.[12-14] There are, however, significant differences. Similarly to the acyclic dienes, the mode of addition during polymerization of PCHD seems to be fixed at the point of entry of the monomer. The preference for the 1,4 mode of addition in apolar noncomplexing solvents is consistent with the formation of a π-type complex between CHD and the covalently bound metal or its tightly bound ion pair prior to the addition of CHD to the growing chain. On the other hand, the 1,2 mode of addition in polar complexing solvents indicates that a strongly solvated ion separated from the growing carbanion[19] prefers to approach the incoming monomer at the point of its highest electron availability, e.g., at carbon 2 or 3 of CHD. However, for all investigated samples of PCHD, the value of $f_{1,2}$ does not exceed 50%. $f_{1,2}$ = 50% seems to represent a limit imposed by steric factors. Inspection of molecular models reveals that the 1,2 mode of addition of CHD to an active center in a 1,2 configuration would require a prohibitively close approach of its methylene protons to those of the ultimate and penultimate units of the growing chain. A long sequence of 1,2 units would be prohibitively crowded. On the other hand, steric hindrance does not seem to be much more severe for intermittent 1,4 and 1,2 addition than for long 1,4 sequences. This is shown schematically in Figure 6.

The effect of temperature revealed by the data in Table III calls for a comment. Surprisingly, the 1,2 addition mode in THF and in DME is favored by an increase in

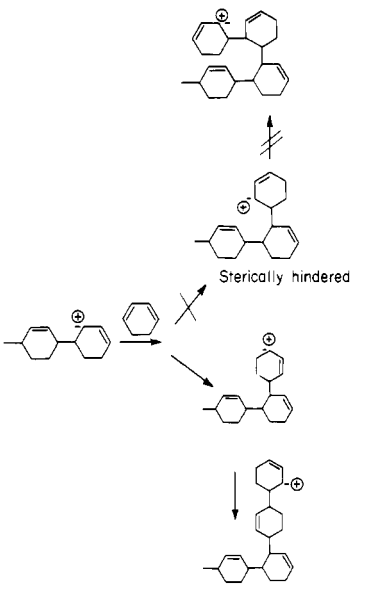


Figure 6. Schematic representation of the severely sterically restricted all-1,2 sequence of a growing PCHD and of an alternating 1,2 and 1,4 sequence.

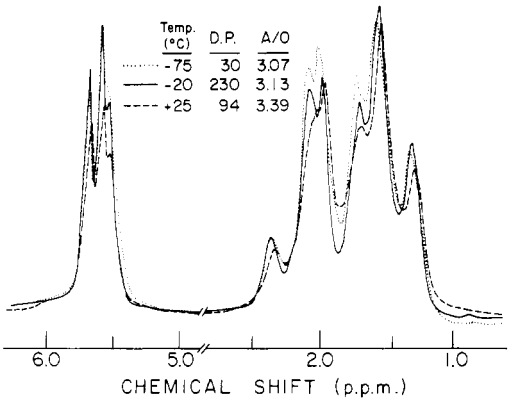


Figure 7. 270-MHz ^1H NMR spectra of PCHD samples prepared in 1,2-DME with sodium naphthalenide as initiator ($CDCl_3$, referred to Me_4Si): (- - -) at +25 °C; (—) at -20 °C; (···) at -75 °C.

temperature and not by its decrease. This trend is evident even from inspection of the unresolved ^1H NMR spectra shown in Figure 7, since the maximum at 1.98 ppm increases and that at 2.07 ppm decreases with increasing temperature. For butadiene and isoprene an opposite and much weaker trend, consistent with an increase in ionic separation with temperature,[18] was observed.[12] Steric hindrance must be again considered to explain the experimentally observed behavior of the CHD system. The increase in segmental mobility with temperature will increase the probability that the growing end will be arranged in a fashion enabling the 1,2 addition during its encounter with the monomer.

The stereoselectivity of polymerizations initiated by Ziegler–Natta and cationic catalysts is much less pronounced than that of anionic systems in apolar solvents. Results in Table III indicate that only ca. 90% of PCHD is in the 1,4 isomeric form for the heptane–$AlEt_3/TiCl_4$ system. The formation of a significant fraction of 1,2 adducts in such a system is indicated by the intensity of the resonance signals in the 127–128-ppm region of its ^{13}C NMR spectrum (cf. Figure 8). Weak absorption signals at ca. 133 ppm may probably be ascribed to the C_2 carbon of the 1,2 isomer. The presence of a significant fraction

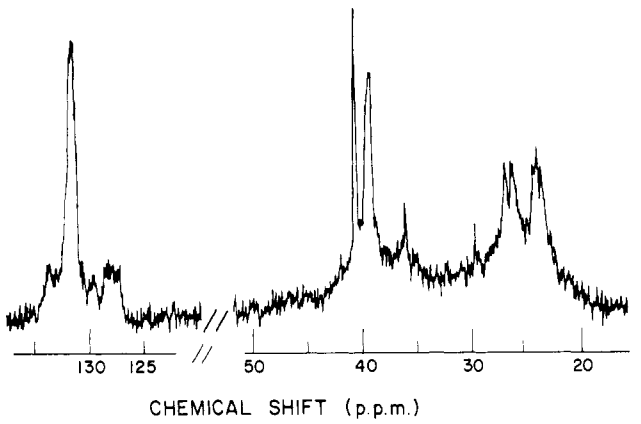


Figure 8. 67.88-MHz proton-decoupled ^{13}C NMR spectrum of the PCHD sample prepared in *n*-heptane with 1/1 $AlEt_3/TiCl_3$ as initiator ($CDCl_3$, referred to Me_4Si).

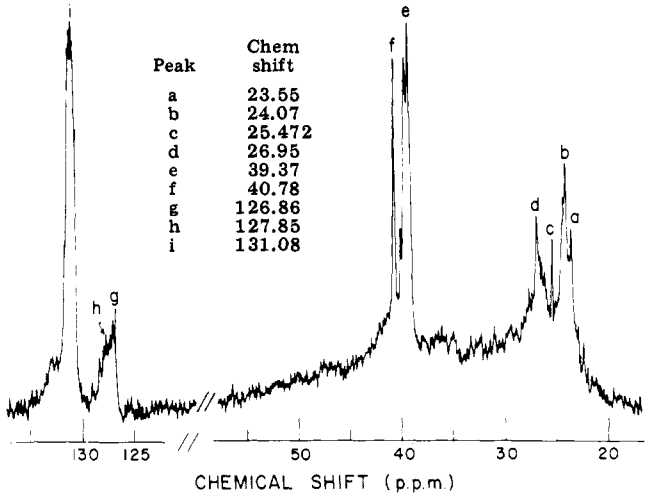


Figure 9. 67.88-MHz proton-decoupled ^{13}C NMR spectrum of the PCHD sample prepared in benzene with $AlCl_3$ as initiator ($CDCl_3$, referred to Me_4Si).

of 1,2 segments in PCHD polymerized cationically in benzene is clearly indicated by the sharp resonance line at 25.47 ppm and by the absorption at 127–128 ppm in its ^{13}C NMR spectrum, shown in Figure 9. A quantitative analysis based on eq 2–5 was, however, not feasible in this case because of the presence of a large fraction of hydrogenated and dehydrogenated rings in this polymer.

The ^{13}C NMR spectra of the investigated samples also provide information about their tacticity. Resonance lines at 130.75 ± 0.05 and 131.13 ± 0.07 ppm are attributed to the olefinic carbons of 1,4-PCHD and those at 26.8 ± 0.1 and 26.32 ± 0.02 ppm to its β carbons. It is obvious that the multiple signals of these carbons in 1,4-PCHD must represent different planomeric forms. Judging by the relative intensities of the resonance lines in Figure 4 (hexane–BuLi system), we ascribe the signal at 131.13 ppm with its two very close neighboring lines to the cis-planomeric segments and the signal at 130.75 ppm to the trans units.

Carbons C_3 and C_6 of 1,4-PCHD (α carbons), which are points of attachment of the cyclohexene rings, should be particularly sensitive to tacticity. Four tacticities are possible for PCHD: erythro diisotactic, threo diisotactic, disyndiotactic, and isosyndiotactic. Four different signals due to α carbons are, indeed, detected in the spectrum shown in Figure 4 (40.65, 39.81, 39.52, and 39.18 ppm). Apparently, segments in all possible modes of tacticity are present in this PCHD, and it may be regarded as virtually atactic. The relative intensities of the lines in Figure 4 suggest that the signal at 40.65 ppm should be ascribed to the threo-diisotactic form, which requires all trans placements. The signals in the 39.5-ppm region should be ascribed to the other tacticities, which require all cis or intermittent cis,trans placements with respect to the plane of the rings.

The differences and similarities between our results and those of previous investigators must be critically discussed at this point. Naumova et al.[9] have stated correctly that anionic polymerization of CHD in bulk leads to formation of 1,4 isomers only. These authors failed, however, to notice formation of mixed 1,4–1,2 isomers in THF. This omission must be attributed to the poor resolution of their ^1H NMR spectra and to their disregarding the effect of partial hydrogenation on the overall intensities of various spectral regions.

Our results confirm those of Lenz and Mango[6] as to the conformations of the PCHD planomers but they disprove their claim that the 1,2 isomers are predominant even in aprotic solvents. The resolution of the NMR spectra of the PCHD's recorded by these authors was poor, and they did not attempt to analyze them in terms of 1,4 or 1,2 isomerism. They based the determination of the isomeric composition of PCHD's on evidence provided by IR spectroscopy. Apparently, they were misled by their implicit assumption that the molar absorptivities of the vibrational modes due to different structural forms do not differ significantly.

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