Two-Dimensional NMR Determination of the Regiosequence Distribution in Polyepichlorohydrin

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ABSTRACT: The microstructure of an amorphous polyepichlorohydrin was investigated using a variety of one- and two-dimensional NMR techniques. Assignments of both the proton and carbon chemical shifts for the four possible regiosequence triads were made. Homo- and heteronuclear coupling constants were determined. From this knowledge, a method of using two-dimensional NMR spectra of PECH to analyze its regiosequence distribution was developed. The method consists of taking a heteronuclear chemical shift correlation spectrum, integrating the peaks corresponding to the regiosequence triads, and calculating the dyad concentrations using first-order Markovian statistics, which were shown to fit the data. The amorphous polyepichlorohydrin studies was found to be ~63% head-to-tail and ~37% head-to-head, tail-to-tail with short blocks of four to five head-to-tail monomer units before a reversal occurs. The results obtained were in good agreement with the other limited data published to date.

Introduction

Polyepichlorohydrin. Polyepichlorohydrin (PECH) is an important industrial elastomer.[1] Most of the industrial polymer is made by the Vandenberg process,[2] which yields a predominantly head-to-tail (H-T) polymer that is often fractionated into crystalline and amorphous fractions with different tacticities. PECH can also be prepared with a variety of other initiators such as the two different ones used to synthesize the highly crystalline and the amorphous PECH examined in this study. The properties and end uses depend partly on the tacticity of the PECH. They also depend on the regiosequence distribution of the PECH. The tacticity and regiosequence distribution of many polymers can be determined fairly easily by proton NMR.[3,4] This method is not applicable to PECH. All five protons of the repeating unit resonate at very similar frequencies, the spin systems are strongly coupled, and the signals from the different sequences overlap greatly. Consequently, until recently its tacticity has been determined mainly by reducing the polymer, with some unavoidable simultaneous degradation, to poly(propylene oxide).[5,6] The latter is somewhat easier to study by NMR, but in the case of atactic poly(propylene oxide) only the isotactic resonances could be assigned unambiguously in its 2D *J*-resolved spectrum.[7] The 2D *J*-resolved spectroscopy experiment is a powerful tool, which often permits measurements of, for example, coupling constants that are obscured in conventional 1D spectroscopy. The tacticity of PECH has also been determined by high-field (90-MHz) ^{13}C NMR without reduction, but with resolution enhancement and curve deconvolution techniques.[8] The purposes of this research were to investigate the microstructure of an amorphous PECH using various NMR techniques and, if possible, to develop a direct NMR method for the characterization of products of epichlorohydrin polymerized with various initiators and under different experimental conditions. Ideally, the method should also be suitable for use with other polymers, which for whatever reason cannot be characterized by conventional proton NMR. This paper describes the results of our investigation and the method for PECH that has been developed as a result.

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NMR. The NMR techniques used for this research included the ^1H and ^{13}C one- and two-dimensional experiments described in the Experimental Section. These various techniques reinforce each other. Agreement among the results greatly increased confidence in the assignments and other results obtained in this study. It would be inappropriate to describe all these techniques in detail here. An interested reader can find information in many sources including refs 9–11.

Experimental Section

Materials. The polyepichlorohydrins (PECH's) used for this study were laboratory products. The crystalline polyepichlorohydrin sample was prepared in diethyl ether using racemic epichlorohydrin (Aldrich Chemical Co., Inc.) and a triethylaluminum (Ethyl Corp.)–water initiator modified with acetylacetone (Aldrich Chemical Co., Inc.) and *l*-borneol (Pfaltz & Bauer, Inc.). The procedure was similar to that used in the Vandenberg process.[2] The product was similar to the highest melting polyepichlorohydrin previously studied by one of us.[12] The whole polymer was used without extraction of any amorphous fraction. Polarimetry showed $[\alpha]^0_D = -10.1°$ in 1-methyl-2-pyrrolidinone at 23 °C. Differential scanning calorimetry at a heating rate of 10 deg/min indicated a melting temperature of 124 °C, which is substantially higher than the melting temperature (117 °C) of the crystalline fraction obtained from the Vandenberg process.[2] Crystallization half times determined by dilatometry as previously described[12] were too fast to measure (<10 min) from room temperature to about 80 °C, ~15 min at 90 °C, and ~95 min at 100 °C. The polymer was shown to be isotactic by comparison of the observed *d* spacings with those reported in the literature for crystalline isotactic polyepichlorohydrin.[13,14] The crystalline polymer was so sparingly soluble in solvents normally used to estimate the molecular weight of PECH's that its molecular weight was not determined. The amorphous cationic polymer was prepared in bulk using triethyloxonium hexafluorophosphate as initiator.[15,16] The polymer studied had a molecular weight of ~40 000 (by size exclusion chromatography, polystyrene calibration) and a glass transition temperature by DSC of −16.7 °C, which is in agreement with that reported earlier.[17]

NMR Spectroscopy. Sample Preparation. Dimethyl sulfoxide-d_6 (DMSO-d_6) from Norell instead of chloroform-d_1 was chosen as the NMR solvent for PECH's. Chloroform-d_1 was undesirable because the ^{13}C chemical shift of chloroform (77.3 ppm) is very close to the chemical shift of the methine group in PECH (78 ppm). Tetramethylsilane (TMS) from Norell was used as the internal reference throughout this study. Solutions (10%) of the selected PECH were prepared by warming the polymer–solvent mixtures under hot tap water.

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Table I. Instrumental Parameter Optimization

NMR experiment	symbol	sweep width, Hz	pulse width, μs	recycle delay time, μs	no. of acquisitions	data points per block × 10^{-3}	data processing	no. of data points	total time, h
one-dimensional proton	^{1}H 1D	±150	4.56 (40°)	500	16	16			
one-dimensional carbon-13	^{13}C 1D	±2273	3.62 (40°)	500	8000	16	*a*		
proton decoupler off during acquisition cationic PECH	PDFA	±2273		500	16000	16	*a*		
distortionless enhancement by polarization transfer cationic PECH	DEPT	±2840		1.5×10^6	128	8	*b*		
two-dimensional homonuclear *J*-resolved cationic PECH		±300 (F_2) ±50 (F_1)		500		32		2000×64^c	4.5
two-dimensional heteronuclear *J*-resolved cationic PECH		±4545 (F_2) ±300 (F_1)		1.0×10^6		32		4000×64^c	1.0
heteronuclear chemical shift correlation catonic and crystalline PECH	HTCSCM	±5291 (F_2) ±841 (F_1)		1.0×10^6		32		4000×48^c	1.2

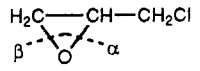
[a] Exponential multiplication function, line broadening factor = 1 Hz. [b] Exponential multiplication function, line broadening factor = 2 Hz. [c] Zero-filled before second Fourier transform.

Instrumentation. NMR spectra were obtained at room temperature using a QE-300 GE NMR spectrometer operating at a proton frequency of 300 MHz and a ^{13}C frequency of 75 MHz. The ^{1}H NMR and ^{13}C NMR were run with a 5-mm ^{1}H/^{13}C switchable probe.

Instrumental Parameter Optimization. The types of NMR experiments performed and their instrumental parameters are given in Table I. The principal information that was gained from each experiment is as follows. PDFA assisted in making assignments and in determining coupling constants. DEPT produced subspectra for methyl, methylene, and methine signals, which confirmed assignments for these groups. The 2D *J*-resolved spectroscopy offered a way to resolve even highly overlapping resonances into readily interpretable multiplets, and permitted some chemical shift assignments and coupling constants to be made in a simple and direct manner. Homonuclear correlation spectroscopy was used to identify spin-coupled pairs of nuclei. HTCSCM, the most useful experiment for the present purposes, permitted identification of all directly bonded carbon–proton pairs in the PECH's, in a time not greatly different from that required for a normal ^{13}C spectral aquisition, and provided data even without any prior knowledge of specific proton assignments. This allowed information from one spectrum to help in the assignment of resonances in other spectra. The Incredible natural abundance double-quantum transfer experiment (INADEQUATE) and long range heteronuclear chemical shift correlated spectroscopy (LRCSCM) were also attempted, but even the optimized spectra for cationic PECH had such poor sensitivity that no additional information could be obtained after 18 h of aquisition.

Results and Discussion

NMR Triads of PECH. Epichlorohydrin (ECH) is a cyclic ether



with one oxygen atom, one methine carbon atom with a chloromethylene substituent, and a methylene carbon atom. Because the methine carbon atom has four different substituents, the monomer exists in both *R* and *S* configurations and can be resolved into pure stereoisomers.[18]

The ring-opening polymerization of ECH can produce PECH, $-[-O-CH(CH_2Cl)-CH_2-]-_n$, with a broad range of microstructures that depend on the mode of ring-opening promoted by the initiator and the optical purity of the monomer. In all cases, each of the backbone carbon atoms of PECH is adjacent to an oxygen atom and the chemical shifts observed in their NMR spectra are shifted accordingly. There are two carbon–oxygen (C–O) bonds in the monomer. The sequence in which the C–O bond

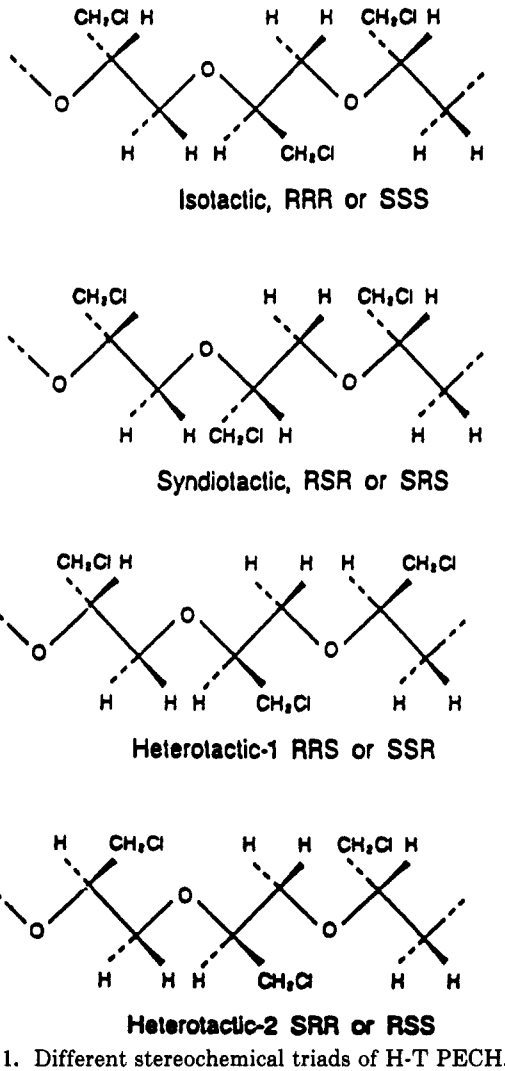


Figure 1. Different stereochemical triads of H-T PECH.

(β or α in the diagram) cleaves during polymerization determines whether the resulting PECH will have a regular head-to-tail (H-T) structure, a regular head-to-head, tail-to-tail (H-H, T-T) structure, or a more random structure. The head is represented as the $-OCH(CH_2Cl)-$ end of the repeat unit, and the tail is represented as the $-CH_2-$ end of the repeat unit. Polymerization of a racemic monomer in a regular H-T manner potentially results in PECH's with the different stereochemical triads shown in Figure 1. In practice only the isotactic crystalline polymer has been prepared. As stated above, the crystalline polymer

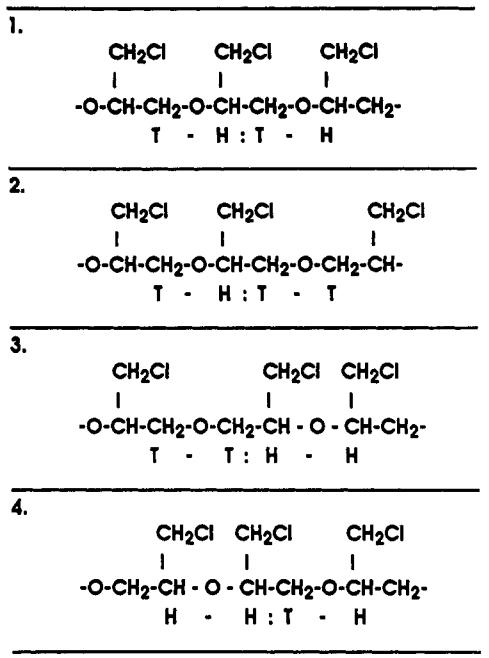


Figure 2. Possible regiosequence triads of PECH.

studied by us had a regular (H-T) isotactic structure with an excess, indicated by its optical activity, of either *-RRR-* or *-SSS-* polymer chains. Regular *RRR...* or *SSS...* chains result in identical NMR spectra. This type of isomerism has been studied repeatedly and is not part of the present work. The crystalline polymer was used as an aid for making assignments of regiosequence resonances in the NMR spectra of the amorphous cationic polymer.

If during the ring-opening polymerization both C–O bonds in ECH are subject to random cleavage, four regiosequence triads are possible for PECH.[19,20] These are illustrated in Figure 2. The regular H-T structural sequence results in the regiosequence triad 1. For simplicity and clarity of labeling to be used below, we have focused on the central monomer unit of the triad and the two adjacent carbon atoms, and have therefore called triad 1 T-H:T-H. That is, a regular H-T structural sequence leads to a T-H:T-H regiosequence triad. If during polymerization, a single, isolated monomer reversal occurs, three additional regiosequence triads result. These are shown in Figure 2 as 2–4 or T-H:T-T, T-T:H-H, and H-H:T-H, respectively, in our designation. The sequences were obtained by reversing the third (right) monomer unit for 2, the second (middle) monomer unit for 3, and the first (left) monomer unit for 4. By use of the techniques described below, NMR assignments for each of these triads have been made and the concentration of each triad has been determined. This new information permits the first calculation directly from NMR data of the percentage of reversed (H-H, T-T) units, in an irregular PECH.

One-Dimensional NMR. One-Dimensional Proton NMR. Proton NMR spectroscopy alone has not been very useful for the determination of the microstructure of a cationic PECH sample.[8,12,21,22] All five protons of the repeating unit of PECH resonate at very similar frequencies, the spin systems are stongly coupled, and because of the different regiosequence diads (H-T, H-H, T-T) in cationic PECH, the ^1H spectrum contains overlapping signals. As a consequence the ^1H spectrum is very difficult to interpret. Two-dimensional NMR techniques to be described below have proven to be much more useful.

One-Dimensional Carbon-13 NMR. The ^{13}C spectra of cationic PECH and crystalline PECH are compared in Figure 3.

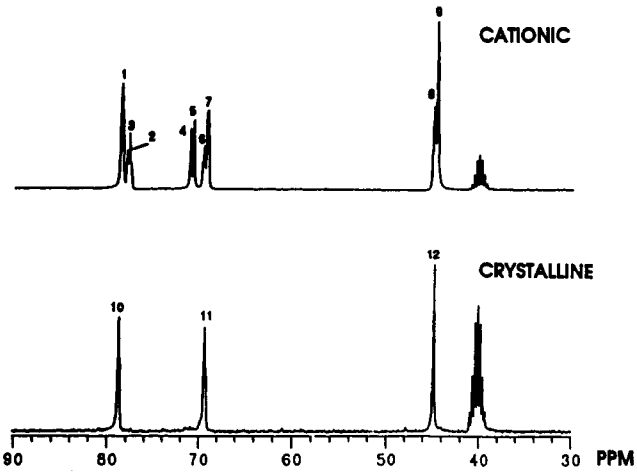


Figure 3. Broad-band proton-decoupled ^{13}C spectra of cationic PECH and crystalline PECH.

The multiple-pulse DEPT technique[23] was employed to separately identify all observed ^{13}C NMR resonances as to carbon atom type, i.e., CH, CH_2, or CH_2Cl carbon atoms. As in previous work,[8] the H-T crystalline polymer leads to three resonances, corresponding to the backbone methine carbon atom (CH: ~78 ppm), the backbone methylene carbon atom (CH_2: ~70 ppm), and the pendant chloromethyl carbon atom (CH_2Cl: ~45 ppm). (The multiplet in the spectrum centered at 40 ppm is due to the solvent DMSO.) The methine, methylene, and chloromethyl carbon atoms all display chemical shift sensitivity to the regiosequence of the polymer chain. The additional triads (T-H:T-T, T-T:H-H, H-H:T-H) of the cationic polymer give rise to structural shifts. The resonance due to the methine group consists of a singlet and a doublet; and the resonance due to the pendant chloromethyl group appears as a doublet. Assignments of the resonances corresponding to H-T units in cationic PECH are made by comparison of the two spectra in Figure 3. The 1, 7, and 9 peaks correspond to backbone methine, backbone methylene, and pendant chloromethyl carbon atoms in H-T PECH, respectively, and their chemical shifts are the same as those of peaks 10–12 in the spectrum of the crystalline polymer.

The chemical shifts of carbon nuclei are sensitive to the presence of neighboring substituents. Carbon substituents α and β to an observed carbon nucleus produce comparable deshielding (~9 ppm), relative to the shielding experienced by an unsubstituted carbon atom.[24] The γ substituents, on the other hand, shield the carbon nucleus with a magnitude that depends on the distance between the observed carbon atom and the γ substituent. The conformationally sensitive γ-effect on ^{13}C NMR chemical shifts has been utilized[25] to predict the chemical shifts observed in polymers, which has facilitated the determination of microstructure. Analysis of such information about the environments of the carbon atoms in cationic PECH has permitted preliminary assignments of chemical shifts of the remaining peaks in the ^{13}C spectrum of cationic PECH. Table II shows the numbers and types of α, β, and γ substituents of backbone methine, backbone methylene, and pendant chloromethyl carbon atoms, respectively, in PECH with different regiosequences.

The salient arguments are as follows.

Peaks 1–3: The backbone methine carbon atom in T-H:T-H has the same number and type of α and β substituents (1 α CH_2, 1 α CH_2Cl, 1 α O, 1 β CH_2, 1 β O) as T-H:T-T and γ substituents very similar (T-H:T-H: 2 γ CH; T-H:T-T: 1 γ CH_2, 1 γ CH) to those of T-H:T-T. This same

Table II. Chemical Environments of the Methine, Methylene, and Chloromethylene Carbon Atoms of PECH in Different Regiosequences

		T-H:T-H	T-H:T-T	T-T:H-H	H-H:T-H
CH	α	CH_2, CH_2Cl, O	CH_2, CH_2Cl, O	CH_2, CH_2Cl, O	CH_2, CH_2Cl, O
	β	CH_2, O	CH_2, O	CH, O	CH, O
	γ	CH, CH	CH_2, CH	CH_2, CH_2, CH_2Cl	CH_2, CH, CH_2Cl
		peak 1	peak 1	peak 2 or 3	peak 2 or 3
CH_2	α	CH, O	CH, O	CH, O	CH, O
	β	CH, CH_2Cl, O	CH_2, CH_2Cl, O	CH_2, CH_2Cl, O	CH, CH_2Cl, O
	γ	CH_2, CH_2, CH_2Cl	CH_2, CH	CH, CH	CH, CH_2, CH_2Cl
		peak 7	peak 4 or 5	peak 4 or 5	peak 6
CH_2Cl	α	CH	CH	CH	CH
	β	CH_2, O	CH_2, O	CH_2, O	CH_2, O
	γ	CH_2, O	CH_2, O	CH, O	CH, O
		peak 9	peak 9	peak 8	peak 8

analysis can be made for T-T:H-H and H-H:T-H regiosequences (Table II). The methine peak at 78.8 ppm (peak 1) probably results from the overlapping of resonances due to T-H:T-H and T-H:T-T regiosequences; the methine peaks at 78.2 ppm (peak 2) and 77.9 ppm (peak 3) correspond to T-T:H-H and H-H:T-H sequences. Not enough information is available to permit a complete analysis of peak 2 and peak 3.

Peaks 4 and 5: The T-H:T-T methylene group and the T-T:H-H methylene have similar chemical environments that are quite different from those of the methylene groups in T-H:T-H and H-H:T-H (Table II). Hence the resonances of the T-H:T-T methylene and the T-T:H-H methylene have similar chemical shifts. The two similar, downfield methylene resonances (peak 4, 71.2 ppm; peak 5, 70.9 ppm) correspond to the T-H:T-T and the T-T:H-H regiosequences. There is not enough information to permit definitive assignments.

Peaks 6 and 7: The H-H:T-H backbone methylene carbon resonance is expected to be similar to the T-H:T-H methylene resonance on the basis of their having the same number and type of α and β subsituents and similar γ substituents. The carbon resonance at 69.4 ppm (peak 7) is known to be due to the T-H:T-H methylene carbon atom. Therefore the next peak downfield (peak 6, 69.7 ppm) would correspond to the resonance due to the H-H:T-H methylene carbon atom.

Peaks 8 and 9: The T-H:T-T chloromethyl group and the T-H:T-H chloromethyl group have the same number and type of α, β, and γ substituents. The resonances due to these carbon atoms overlap at 44.7 ppm (peak 9). The T-T:H-H chloromethyl and the H-H:T-H chloromethyl groups have the same number and type of α, β, and γ substituents. Therefore the resonances due to these carbon atoms overlap at 45.0 ppm (peak 8).

The ^{13}C NMR chemical shifts and the corresponding regiosequence assignments are shown in Table III. This interpretation of the ^{13}C NMR spectra has been confirmed by the 2D HTCSCM experiments described below.

Proton Decoupler off During Acquisition. The PDFA spectrum and proton-decoupled ^{13}C spectrum of cationic PECH are shown in Figure 4. In the ^{13}C spectrum the peak for the backbone methine carbon atom coupled to one proton is split into a doublet. The backbone methylene carbon atom coupled to two protons is split into a triplet. Because the coupling constant, J, is greater than the difference of the chemical shifts, the methylene peaks in the PDFA spectrum overlap and appear as a pseudoquartet. The pendant chloromethyl carbon atom

Table III. ^{13}C NMR Chemical Shifts, Regiosequence Assignments, and C–H Coupling Constants for Cationic PECH

resonance	chemical shift, ppm	assignment	J_{C-H}, Hz
1	78.8 (overlap)	CH: T-H:T-H / T-H:T-T	145.4
2	78.2	CH: T-T:H-H or H-H:T-H	140.6
3	77.9	CH: T-T:H-H or H-H:T-H	140.6
4	71.2	CH_2: T-H:T-T or T-T:H-H	145.4
5	70.9	CH_2: T-H:T-T or T-T:H-H	143.0
6	69.7	CH_2 H-H:T-H	145.4
7	69.4	CH_2 T-H:T-H	143.0
8	45.0 (overlap)	CH_2Cl: T-T:H-H / H-H:T-H	154.8
9	44.7 (overlap)	CH_2Cl: T-H:T-H / T-H:T-T	154.8

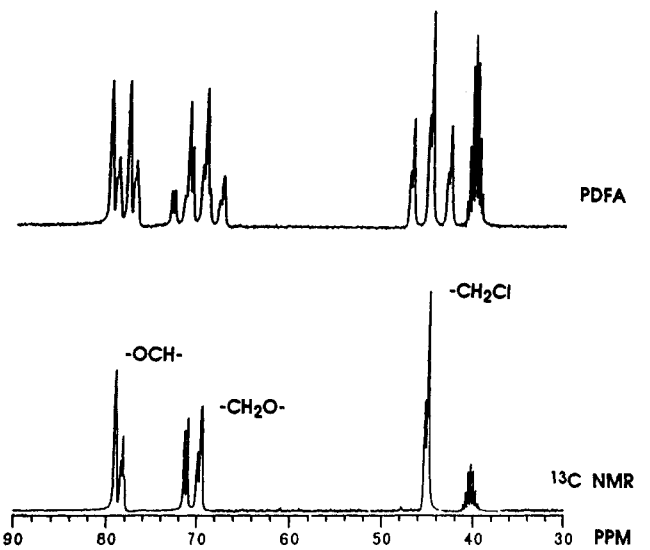


Figure 4. PDFA spectra of cationic PECH.

coupled to two protons is split into a triplet. The PDFA spectrum is consistent with the result from the DEPT experiment mentioned previously. The one-bond heteronuclear (C–H) coupling constants, $^1J_{CH}$, measured from PDFA, were 139.8 ± 0.2, 141.5 ± 0.2, and 153.1 ± 0.2 Hz for CH, CH_2, and CH_2Cl, respectively. Long range coupling constants were not determined because of the extensive overlap present in the PDFA spectrum.

Two-Dimensional NMR. 2D NMR was very helpful in confirming the above preliminary assignments and allowed a quantitative estimate of the amounts of each triad.

Homonuclear 2D *J*-Resolved. The homonuclear 2D *J*-resolved experiment was employed to resolve the highly overlapping resonances in the proton spectrum. From the tilted spectrum of the cationic PECH the proton–proton coupling constants and proton chemical shifts can be determined. The tilted *J*-resolved spectrum for cationic PECH with coupling shown is presented in Figure 5. In Figure 5, peaks 1 and 2 refer to the CH_2Cl protons, and peaks 3 and 4 refer to the CH proton and CH_2 protons, respectively, of the PECH repeat unit. The protons of

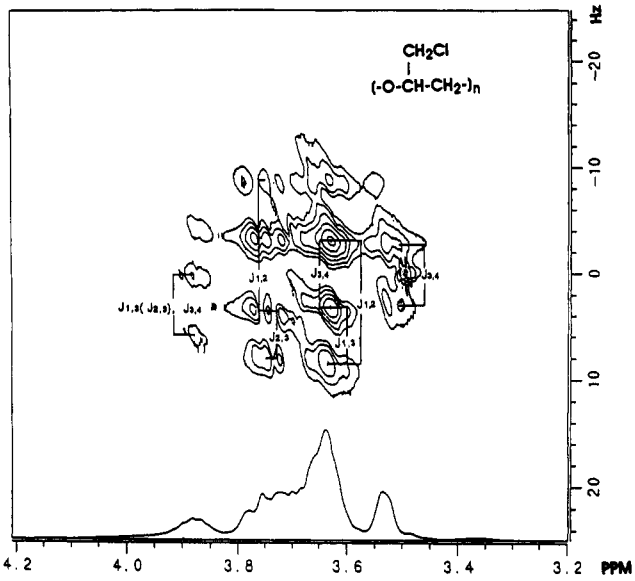


Figure 5. Tilted 2D homonuclear J-resolved spectrum of cationic PECH showing H–H coupling constants. 1 and 2 refer to the CH_2Cl protons. 3 refers to the CH proton, and 4 refers to the CH_2 protons.

the backbone CH_2 for the T-H:T-T and T-T:H-H sequence resonate at 3.5 ppm. The slice of the 2D spectrum at this frequency is shown in Figure 6a. This doublet arises from coupling of the methylene protons with the backbone CH proton. The coupling constant $J_{3,4}$ was determined to be 6.7 Hz. The resonance of the CH_2 protons for the T-H:T-H and H-H:T-H sequence appears at 3.6 ppm and overlaps with the resonance due to one of the nonequivalent CH_2Cl protons. The coupling by the CH proton causes the resonance due to the CH_2 protons to split into a doublet, which is shown in Figures 5 and 6b ($J_{3,4}$). The coupling constant $J_{3,4}$ was found to be 6.4 ppm. The two protons of the CH_2Cl group are magnetically nonequivalent. They resonate at 3.6 and 3.8 ppm. The slices at 3.6 and 3.8 ppm are shown in Figures 6b,c, respectively. In addition to the coupling between the two nonequivalent protons of the CH_2Cl group ($J_{1,2}$) there are also couplings of the CH proton with the CH_2Cl protons ($J_{1,3}$, $J_{2,3}$). The $J_{1,3}$ and $J_{2,3}$ couplings are equal. This causes the resonance due to the CH_2Cl protons to be split into a pseudoquartet in the 2D J-resolved spectrum. The coupling constant between the nonequivalent CH_2Cl protons ($J_{1,2}$) was determined to be 11.8 Hz. The coupling constants for interaction between the CH_2Cl protons and the CH proton ($J_{1,3}$, $J_{2,3}$) were found to be 5.6 Hz. The resonance due to the CH_2Cl proton for T-H:T-H and T-H:T-T sequences appears at 3.7 ppm. The resonance at 3.7 ppm overlaps extensively with that due to other protons. The resonance due to the CH proton for H-H:T-H and T-T:H-H sequences appears at 3.9 ppm. The CH proton is coupled with the two CH_2Cl protons and the two CH_2 protons. Because the magnitudes of $J_{1,3}$ ($J_{2,3}$) and $J_{3,4}$ are quite similar, the CH proton resonance is split into a pseudoquintet in the 2D J-resolved spectrum. The intensity of the two smaller side peaks of the pentet is too low to permit them to be seen in the 2D spectrum. In the slice which is shown in Figure 6d, the resonance due to the CH proton resonance appears as a pseudopentet.

Table IV summarizes the proton chemical shifts and some proton–proton coupling constants for the CH, CH_2, and CH_2Cl groups in the different regiosequences.

Heteronuclear 2D J-Resolved. In heteronuclear 2D J-resolved spectroscopy, couplings and chemical shifts are separately observed in the two dimensions. The multiplicity caused by proton coupling appears in F_1, and the proton-decoupled ^{13}C chemical shifts appear in F_2. Because the decoupler is gated off only during the second half of the evolution period, the heteronuclear coupling constants appear as $J/2$ rather than J in the F_1 dimension. The heteronuclear 2D J-resolved experiment of cationic PECH is shown in Figure 7. From the J-resolved spectrum, ^{13}C chemical shifts and coupling constants for different regiosequences in cationic PECH can be accurately determined. The chemical shifts and coupling constants

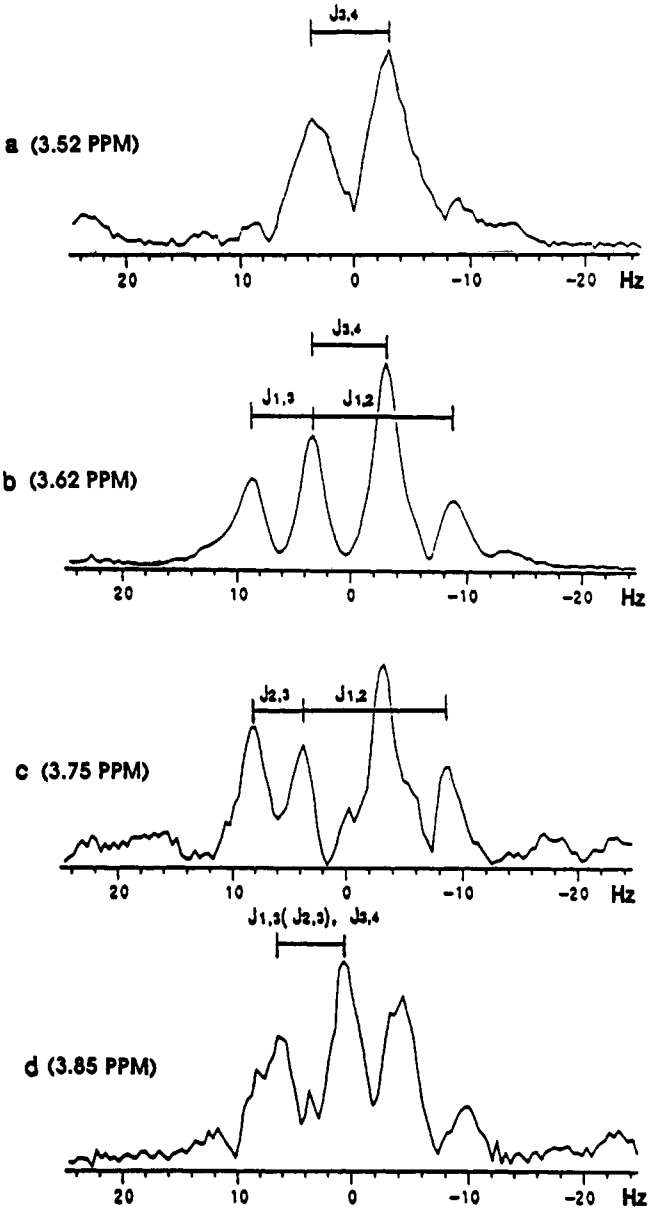


Figure 6. Slices of the homonuclear 2D J-resolved spectrum of cationic PECH.

Table IV. Proton Chemical Shifts and H–H Coupling Constants for Different Regiosequences of PECH

proton	assignment	chemical shift,[a] ppm	coupling constant,[a] Hz
	T-H:T-H and T-H:T-T	$\delta_1 = 3.62$	
CH_2Cl			$J_{1,2} = 11.8$
	T-T:H-H and H-H:T-H	$\delta_2 = 3.75$	
	T-H:T-H and H-H:T-H	$\delta_4 = 3.62$	$J_{3,4} = 6.4$
CH_2			
	T-T:H-H and T-H:T-T	$\delta_4 = 3.51$	$J_{3,4} = 6.7$
	T-H:T-H and T-H:T-T	$\delta_3 = 3.66$	
CH			$J_{1,3} = J_{2,3} = 5.6$
	T-T:H-H and H-H:T-H	$\delta_3 = 3.85$	

[a] 1 and 2 refer to the CH_2Cl protons. 3 refers to the CH proton, and 4 refers to the CH_2 protons.

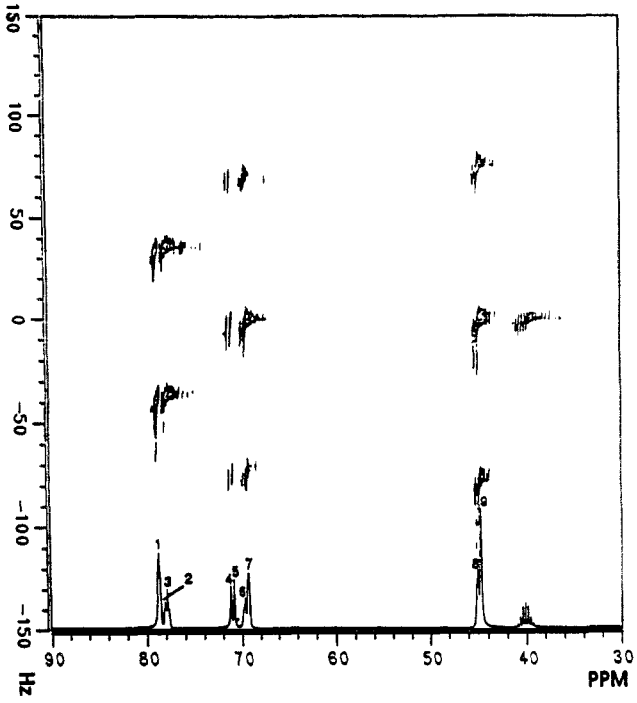


Figure 7. Heteronuclear 2D J-resolved spectrum of cationic PECH.

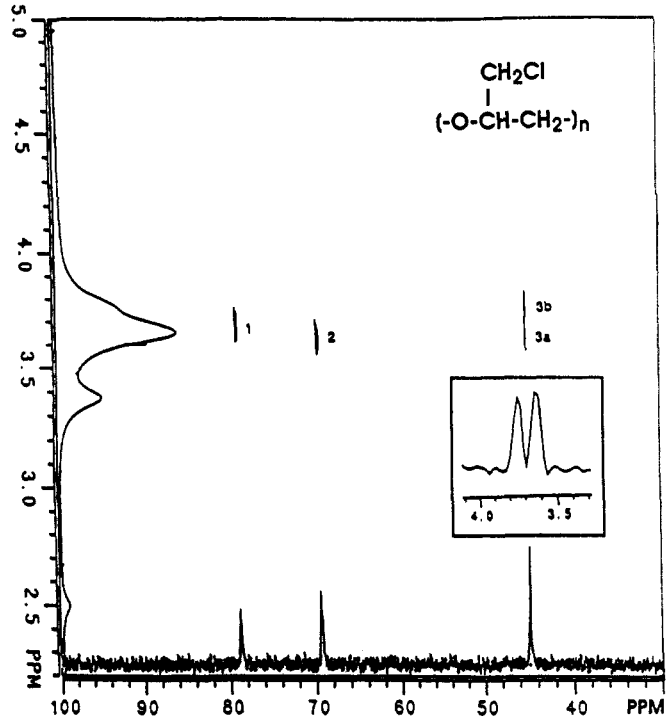


Figure 8. Heteronuclear shift correlation (HTCSCM) spectrum of crystalline cationic PECH. The insert shows slices of the peak, ^{13}C at 44.85 ppm, arising from the resonance due to the pendant CH_2Cl group in the 2D HTCSCM spectrum.

for cationic PECH from the heteronuclear 2D J-resolved experiment agree with those obtained from the proton-decoupled ^{13}C NMR spectrum and the PDFA experiment and are the same as those given in Table III.

Heteronuclear Chemical Shift Correlation. The HTCSCM experiment represents one of the most powerful applications of 2D NMR to date. It provides both carbon and proton chemical shifts at the same time, and more important, it establishes a one-to-one correspondance for each pair of directly bonded carbon and hydrogen atoms. The HTCSCM spectrum of crystalline PECH is shown in Figure 8. The proton-decoupled ^{13}C chemical shifts are along the F_2 axis, and proton-decoupled proton chemical shifts are along the F_1 axis. In the HTCSCM spectrum of crystalline PECH, peak 1 corresponds to the backbone CH of T-H:T-H. The ^{13}C chemical shift is 78.8 ppm, and the proton chemical shift is 3.66 ppm. Peak 2 corresponds to the backbone CH_2 of T-H:T-H. The ^{13}C chemical shift is 69.4 ppm, and the proton chemical shift is 3.62 ppm. In the repeat units of PECH, the backbone CH is a chiral center. Therefore, the two protons of the pendant CH_2Cl are magnetically nonequivalent. The CH_2Cl peak splits into a doublet. Peaks 3a and 3b in Figure 8 correspond to the pendant CH_2Cl. The slice of peaks 3a and 3b of the 2D HTCSCM spectrum is shown in the insert in Figure 8. The ^{13}C chemical shift of CH_2Cl is 44.7 ppm. The proton chemical shifts of peaks 3a and 3b are 3.62 and 3.74 ppm, respectively. The chemical shift assignments of crystalline PECH are shown in Table V.

Table V. ^{13}C and ^{1}H Chemical Shifts for Crystalline PECH in the HTCSCM Spectrum

resonance	^{13}C, ppm	^{1}H, ppm	assignment	
1	78.8	3.66	CH	T-H:T-H
2	69.4	3.62	CH_2	T-H:T-H
3a		3.62		
	44.7		CH_2Cl	T-H:T-H
3b		3.75	(nonequivalent)	

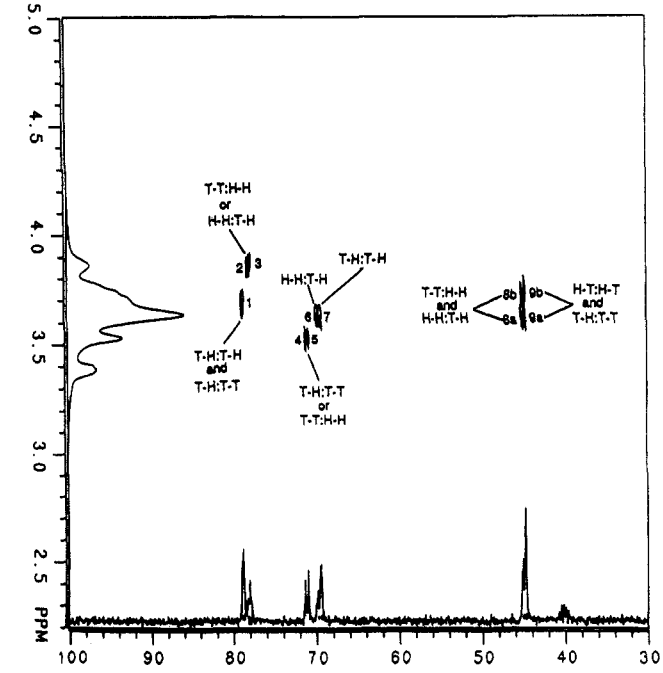


Figure 9. Heteronuclear chemical shift correlation (HTCSCM) spectrum of cationic PECH with proton chemical shifts and regiosequence assignments.

The 2D HTCSCM spectrum of cationic PECH is shown in Figure 9. From comparison of this spectrum with the HTCSCM of crystalline PECH (Figure 8) and from the previous analysis, the proton and carbon chemical shift assignments for different regiosequences can be assigned unambiguously. The HTCSCM spectrum of cationic PECH with proton chemical shifts and regiosequence assignments is shown in Figure 9. In Figure 9, peak 1 arises from an overlap of the CH resonances due to T-H:T-H and T-H:T-T sequences. Peak 7 corresponds to the CH_2 resonance of T-H:T-H, and peak 6 corresponds to the same resonance for H-H:T-H. Peaks 8a and 8b result from the overlapping of resonances corresponding to the CH_2Cl group of T-T:H-H and H-H:T-H. Peaks 9a and 9b are due to overlapping chloromethyl resonances of T-H:

Table VI. ^{1}H Chemical Shifts, Regiosequence Assignments, and Integration Data for the HTCSCM Spectrum of Cationic PECH

resonance	chemical shift, ppm	assignment		integration (±2%)
1	3.66 (overlap)	CH	T-H:T-H T-H:T-T	64 (overlap)
2	3.85	CH	T-T:H-H or H-H:T-H	36
3	3.86	CH	T-T:H-H or H-H:T-H	
4	3.51	CH_2	T-H:T-T or T-T:H-H	18
5	3.51	CH_2	T-H:T-T or T-T:H-H	17
6	3.62	CH_2	H-H:T-H	20
7	3.62	CH_2	T-H:T-H	45
8a	3.62 (overlap)	CH_2Cl	T-T:H-H	36 (overlap)
8b	3.75	CH_2Cl	H-H:T-H	
9a	3.62 (overlap)	CH_2Cl	T-H:T-H	64 (overlap)
9b	3.75	CH_2Cl	T-H:T-T	

Table VII. Concentration of Regiosequence Triads in Cationic PECH

regiosequence triad	concn (±2%)	regiosequence triad	concn (±2%)
T-H:T-H	45	T-T:H-H	17–18
H-H:T-H	20	T-H:T-T	17–18

T-H and T-H:T-T sequences. The a, b splitting of peaks 8 and 9 in the proton spectrum is directly due to the two magnetically nonequivalent protons of CH_2Cl and is independant of different regiosequences. The proton chemical shifts and regiosequence assignments of cationic PECH are shown in Table VI.

The integration of each peak due to the different regiosequences in cationic PECH was performed on the HTCSCM spectrum. From the integration data, the concentration of each regiosequence in cationic PECH was determined and is shown in Table VI. As can be seen in Table VI, there is about 45% of the T-H:T-H (peak 7) regiosequence and about 20% of the H-H:T-H (peak 6) regiosequence. The concentration of the other two regiosequences, T-H:T-T and T-T:H-H, is between 17 and 18%. Peak 1 (64%) arises from an overlap of the CH resonance of the T-H:T-H regiosequence (45%) with the resonance due to T-H:T-T for which the concentration is about 19%. The integration sum of peaks 2 and 3 is 36%, which is lower than the concentration of T-H:T-H (45%). Therefore, peaks 2 and 3 would correspond to the CH of two regiosequences which do not include T-H:T-H. According to the previous analysis, these two regiosequences are T-T:H-H and H-H:T-H. Peaks 8a and 8b are due to the nonequivalent protons of the CH_2Cl group for which the integration sum is 64%. They correspond to an overlap of resonances due to the T-H:T-H (45%) and T-H:T-T (17–18%) sequences. The integration sum for peaks 9a and 9b is 36%. The 9a and 9b peaks are due to overlapping chloromethyl resonances of T-T:H-H and H-H:T-H sequences. Table VII summarizes the concentrations of each of the regiosequence triads in our cationic PECH sample.

Long Range Heteronuclear Chemical Shift Correlation. A long range HTCSCM experiment was optimized and performed several times to try to establish three-bond long range proton–carbon connectivities. Although, in theory, this is the ideal experiment to determine such connectivities, in practice, it failed to yield any useful information. Because of the short carbon relaxation times (ca. 0.1–0.2 s) and the long delays inherent in this experiment, no significant data were obtained, even with 2 days of acquisition. Moreover, the overlap of the proton chemical shifts makes it impossible to identify the direct coupling.

Structure of Cationic PECH. Analysis of the experimentally determined concentrations of the regiosequence triads in cationic PECH leads directly to knowledge about the regularity of the PECH chains thereof. Note that the ^{1}H NMR spectra at 300 MHz and the ^{13}C spectra at 75 MHz are not sensitive enough to resolve the different stereosequence triads in PECH, but as shown above, they are well suited for resolving the different regiosequence triads by the methods described here. This is no reason to doubt that applying similar techniques to spectra obtained at sufficiently higher resolution would permit analysis of the stereoregularity of PECH as well. As stated in the introduction, the purpose at this stage was to examine the regiosequence distribution in PECH. Accordingly, the analysis that follows applies only to regiosequences even though the methods used have most frequently been applied by previous workers in the field to analysis of stereoregularity.[3,4,8,26–28] The differences are that in our treatment we use as variables head-to-tail (H-T) instead of isotactic or meso and head-to-head, tail-to-tail (H-H, T-T) instead of syndiotactic or meso. The mathematical treatment is the same unless otherwise noted.

Assuming a purely random process of ring-opening of the α and β bonds of racemic monomer and assuming the configuration of the entering repeat unit is independent of the configuration of the growing chain end, the Bernoulli model leads to the following probabilities:

for dyads:	P_β	for H-T
	$P_\alpha = (1 - P_\beta)$	for H-H, T-T
for triads:	P_β^2	for (T-H:T-H)
	$2P_\beta(1 - P_\beta)$	for (T-H:T-T) + (H-H:T-H)
	$(1 - P_\beta)^2$	for (T-T:H-H)

where P_β and P_α are the probabilities of ring-opening of the β and α bonds, respectively. As usual for a purely random chain, the probabilities for all triads are equal; i.e., if cationic PECH had purely random sequences, the triad probabilities would be (T-H:T-H) = (T-H:T-T) = (H-H:T-H) = (T-T:H-H) = 0.25, and the dyad probabilities would be $P_\beta = P_\alpha = 0.50$. As shown in Table VII, this is clearly not true for the triads of cationic PECH. Moreover, P_β and P_α, calculated from the regiosequence triad data, are 67% and 33%, respectively. Our cationic PECH does not fit the Bernoulli Model. Our crystalline PECH would fit the Bernoulli Model, but since for this polymer $P_\beta = 1$, this is a limiting case and could fit other models as well.

Numerically, the P_β and P_α data are more like the results shown in Table VIII for poly(propylene oxide)s (PPO's) and PECH's, for which steric control of the entering monomer unit by the last unit of the growing chain end was demonstrated.[8,26–28] A first-order Markov sequence would be generated by propagation steps in which the mode of addition of the approaching monomer is influenced by whether the growing chain end is H-T or H-H, T-T. The choice depends on the outcome of the previus addition. Two conservation relationships and two independent

Table VIII. Tacticity of Some Polyoxiranes Prepared with Different Initiators

		tacticity in %					
		dyads[a]		triads[b]			
polymer	initiator	i	s	I	H	S	ref
PPO	TPPAlCl[c]	67	33	45	42	13	28
PPO	TPPAlCl[c]	69	31	47	43	10	26
PPO	$Zn(OMe)_2$	67	33	51	32	17	27
PECH1	Vandenberg[d]	52[e]	48[e]	25[f]	47	29	8
PECH2	Vandenberg[d]	54[e]	46[e]	34[f]	40	27	8
PECH3	Vandenberg[d]	61[e]	39[e]	44[f]	36	22	8
PECH4	Vandenberg[d]	90[e]	10[e]	84[f]	12	4	8

[a] i and s correspond to isotactic and syndiotactic, respectively, in dyad sequences. [b] I, H, and S correspond to isotactic, heterotactic, and syndiotactic, respectively, in triad sequences. [c] (Tetraphenylporphinato)aluminum chloride. [d] Triethylaluminum–0.6 water followed by fractionation of the resulting PECH into four fractions, PECH1, PECH2, PECH3, and PECH4, using acetone. [e] Calculated from the data of Cheng and Smith.[8] [f] From the methylene carbon atom resonance.

probabilities characterize such a system:[4]

$$P_{\beta/\beta} + P_{\beta/\alpha} = 1$$

$$P_{\alpha/\alpha} + P_{\alpha/\beta} = 1$$

$$P_{\beta/\alpha} = \frac{\text{(T-H:T-T)} + \text{(H-H:T-H)}}{2\text{(T-H:T-H)} + \text{(T-H:T-T)} + \text{(H-H:T-H)}}$$

$$P_{\alpha/\beta} = \frac{\text{(T-H:T-T)} + \text{(H-H:T-H)}}{2\text{(T-T:H-H)} + \text{(T-H:T-T)} + \text{(H-H:T-H)}}$$

To test a given system, the quantity $(P_{\beta/\alpha} + P_{\alpha/\beta})$ is calculated from the experimental triad data. This quantity may vary from 0 to 2. When a given system is tested using these relationships, several different results may be obtained. They include:

$P_{\beta/\alpha} + P_{\alpha/\beta} = 1$	system is Bernoullian (strictly random β or α ring-opening)
$P_{\beta/\alpha} = P_{\alpha/\beta} = 0$	infinitely long blocks of H-T or H-H, T-T structures or a mechanical mixture of the two types of chains (all β or all α ring-opening) occurs
$P_{\beta/\alpha} + P_{\alpha/\beta} < 1$	system tends toward a blocklike structure (sequences of β ring-opening with occasional α ring-opening sequences)
$P_{\beta/\alpha} = P_{\alpha/\beta} = 1$	regularly alternating β and α ring-opening occurs
$P_{\beta/\alpha} + P_{\alpha/\beta} > 1$	there is a tendency for alternating β and α ring-opening to occur[4]

When this test is applied to the experimental data for cationic PECH in Table VII, $P_{\beta/\alpha} = 0.296$, $P_{\alpha/\beta} = 0.513$, and $(P_{\beta/\alpha} + P_{\alpha/\beta}) = 0.809$. By this test, since $(P_{\beta/\alpha} + P_{\alpha/\beta}) < 1$, the system is not Bernoullian, but instead tends toward a blocklike structure. Further attempts to fit the observed triad data indicate that, on average, during our cationic polymerization, an α ring-opening reaction occurred after four to five β ring-opening reactions. Again the crystalline PECH is a special case of first-order Markovian statistics. Since $P_{\beta/\alpha} = P_{\alpha/\beta} = 0$, infinitely long blocks of H-T or H-H, T-T are indicated. This is consistent with what was already known about this model PECH, which is 100% H-T within experimental error. The success of the first-order Markovian test indicates that the mode of addition of an approaching monomer is influenced by the configuration of the growing chain end. This is in agreement with an earlier suggestion that cationic polymerization of ECH involves participation of the growing chain end in the transition state.[16,29] It is also in agreement with the observations of Cheng and Smith,[8] who studied tacticities of four different PECH's made via Vandenberg's process[2] and found that $P_{m/r} + P_{r/m} < 1$ for each of them. That is, the observed tacticities also fitted statistics indicating that the configuration of the incoming monomer unit is influenced by the configuration of the growing chain end. For first-order Markovian statistics, P_β and P_α can be calculated from the following relationships with the observed triads for cationic PECH:

$$P_\beta = \frac{P_{\alpha/\beta}}{P_{\alpha/\beta} + P_{\beta/\alpha}} = 0.63$$

$$P_\alpha = \frac{P_{\beta/\alpha}}{P_{\beta/\alpha} + P_{\alpha/\beta}} = 0.37$$

First-order Markovian statistics in the case of ring-opening polymerization of a mixture of enantiomers has also been analyzed as a particular case of copolymerization.[3,28] The method is applicable for analysis of stereosequence data where indeed two enantiomers compete for ring-opening during polymerization with only β-cleavage of the ring. The method does not apply as well for our purposes, where we are studying the relative rates of two different ways of ring-opening, β and α, of the monomer.

Conclusions

A method of using 2D NMR spectra of PECH to analyze its regiosequence distribution has been developed. It consists of taking its HTCSCM spectrum, integrating the peaks corresponding to the regiosequence triads, and calculating the dyad concentrations using first-order Markovian statistics. In this study assignments of both the proton and carbon chemical shifts for the four possible regiosequence triads have been made. The ^{13}C chemical shifts are in good agreement with those previously made by Cheng and Smith.[8] Proton chemical shifts have not been reported previously. From integration of the peaks in the HTCSCM spectrum, the concentration of each regiosequence in our cationic PECH was calculated. When these experimental triads were tested by first-order Markovian statistics, a fit was found for a polymer with short blocks of four to five monomer units resulting from β-cleavage of the ECH (H-T PECH) and the rest of the monomer units from α-cleavage of the ECH (H-H, T-T PECH). The cationic PECH was found to be ~63% H-T and ~37% H-H, T-T.

To reach these conclusions a variety of one-dimensional and two-dimensional NMR spectra of our cationic PECH were obtained and analyzed. Similar spectra of a crystalline PECH aided in the analysis and simplified assignment of some peaks. The DEPT experiment provided information for CH, CH_2, and CH_2Cl peak identification. ^{13}C spectroscopy allowed basic assignment of the four regiosequence triads in cationic PECH. From two-dimensional J-resolved experiments, the heteronuclear coupling constants (J_{C-H}) and homonuclear coupling constants (J_{H-H}) were determined and proton chemical shifts were assigned for different regiosequences. From the HTCSCM experiment, absolute proton assignments were correlated with their respective ^{13}C assignments. Chemical shifts and coupling constants for cationic PECH derived from the proton decoupled ^{13}C NMR spectrum, a PDFA experiment, and heteronuclear 2D J-resolved spectroscopy were in good agreement.

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