Stereoconfigurations of Poly(vinyl bromide) and Poly(vinyl chloride). An Examination by Carbon-13 NMR of the Effects of Temperature and *n*-Butyraldehyde

R. E. Cais* and W. L. Brown

Bell Laboratories, Murray Hill, New Jersey 07974. *Received December 21, 1979*

ABSTRACT: Carbon-13 NMR has been used to determine the stereoconfigurations in poly(vinyl bromide) and poly(vinyl chloride) samples prepared by bulk, free-radical polymerizations at temperatures from −78 to +100 °C. The T_1 values for poly(vinyl bromide) at 80 °C were 0.16 s for the methine carbon and 0.09 s for the methylene carbon. The configurational splittings in the spectra were assigned by NMR studies of the model compound 2,4-dibromopentane. Poly(vinyl bromide) and poly(vinyl chloride) have Bernoullian stereosequence distributions, with differences in activation enthalpies for meso vs. racemic placement of 1.27 ± 0.03 and 1.09 ± 0.02 kJ/mol, respectively. These values were strongly influenced when the polymerizations were conducted in *n*-butyraldehyde, which further lowered the free energy of racemic placement with respect to meso placement by 0.20 and 0.57 kJ/mol for poly(vinyl bromide) and poly(vinyl chloride), respectively. The aldehyde-modified polymers have low degrees of polymerization, with end groups resulting from initiation and termination involving *n*-butyraldehyde.

Although the microstructure of poly(vinyl chloride) has been elucidated in great detail, particularly since the advent of carbon-13 NMR,[1-3] there are no comparable studies of poly(vinyl bromide), reflecting in part its relative commercial insignificance. In view of recent work aimed at understanding the stereoconfigurational splittings in the carbon-13 NMR spectra of poly(vinyl chloride) in terms of three-bond gauche or γ interactions,[4] it seemed interesting to us to examine the next higher homologue of the poly(vinyl halides), in order to contrast the γ effects of bromine and chlorine.

The dependence of polymer stereoconfiguration or tacticity on polymerization temperature would also highlight the difference in steric influence of bromine and chlorine as backbone substituents. Early proton NMR studies of poly(vinyl bromide) have not been conclusive, however, although they have established that the polymer is atactic, with a probable bias in favor of syndiotactic dyads.[5,6] The effect of temperature over the range 0–80 °C was also investigated by proton NMR,[7] but the data are subject to considerable interpretive error because of the poor resolution of peaks from discrete configurational sequences.

Despite far greater effort the situation is not much better for poly(vinyl chloride), for which reported values of the difference in activation enthalpy for isotactic vs. syndiotactic placement range from about 0.84 to 2.5 kJ/mol (the relevant literature is summarized in ref 8). This range of values underscores the imprecision of the proton NMR method as a routine analytical tool for determining the tacticity of poly(vinyl chloride).[9]

The effect of solvents, and specifically *n*-butyraldehyde, on the tacticity of poly(vinyl chloride) is likewise an area of controversy. Whereas infrared[10] and NMR[11] evidence has suggested to some authors that polymers prepared in *n*-butyraldehyde have an enhanced syndiotactic content, which is also consistent with the crystallinity revealed by X-ray diffraction patterns,[12,13] other authors have refuted these claims on the basis of proton NMR.[14] Also, it has been suggested that the crystallinity is due to a lower molecular weight and branch content,[13,15] rather than increased stereoregularity. Unfortunately, in the only carbon-13 NMR spectra of butyraldehyde-modified poly(vinyl chloride) published to date, the signal-to-noise ratio is not satisfactory for a clear resolution of the issue.[16]

In the present study the tacticities of poly(vinyl bromide) and poly(vinyl chloride) samples prepared by bulk, free-radical polymerizations at temperatures from −78 to +100 °C have been measured by carbon-13 NMR. The structural resolution afforded by this probe has allowed reliable conclusions to be drawn in the aforementioned areas. It is shown unequivocally that *n*-butyraldehyde exerts a strong regulating influence on the tacticity of poly(vinyl chloride), with a similar but reduced effect on poly(vinyl bromide). Carbon-13 chemical shifts are reported as a function of concentration, solvent, and temperature for meso and racemic 2,4-dibromopentanes, which are the simplest models of stereosequence dyads in poly(vinyl bromide).

Experimental Section

Vinyl bromide and vinyl chloride were purchased from Matheson Gas Products. The monomers were dried by passage through activated molecular sieves (Linde 3A), distilled under vacuum, and freed from traces of air by pumping during repeated freeze–thaw cycles. Aldrich Chemical Co. supplied *n*-butyraldehyde, which was degassed and fractionally distilled under high vacuum. Commercial azobis(isobutyronitrile) and 1,1′-azobis(1-cyclohexanenitrile) initiators were used as received.

Polymerizations were conducted in heavy-wall glass ampules, which had been sealed under vacuum after addition of known amounts of monomer, initiator, and solvent, where necessary. Initiation at temperatures of 0 °C or lower was provided by cobalt-60 γ radiation with an effective dose rate of 0.34 Mrd/h. Temperature was maintained in thermostatically regulated baths or, in the experiments involving radiation initiation, by baths containing ice–water (0 °C), chlorobenzene slush (−45 °C), and equilibrated dry ice–acetone mixtures (−78 °C).

After a suitable conversion to polymer was achieved, the ampule was placed in liquid nitrogen, cut open, and transferred to an apparatus where the unreacted monomer could be vented through a series of aqueous potassium permanganate solutions for disposal. The residual polymer was washed repeatedly with methanol, dissolved when possible in an acetone–carbon disulfide mixture, precipitated by excess methanol, and dried under vacuum at 50 °C for about 15 h.

Carbon-13 NMR spectra were recorded at 22.62 MHz on a Bruker WH-90 spectrometer. Typical conditions were as follows: 30 000 scans, 12.6-μs pulse width (90° flip angle), 3.0-s pulse spacing, 2.5-kHz sweep width, 4K data points for the real spectrum, broad-band proton decoupling, 1.0 g of polymer in 3 cm^3 of solution, and internal Me_4Si as reference. A pulse spacing of 10.0 s was used for end-group and model compound studies.

The model compound 2,4-dibromopentane was obtained from Columbia Organic Chemicals and used without further purification (carbon-13 NMR indicated a purity of better than 99%). The proton NMR spectrum at 60 MHz, recorded at room temperature with a 50% by volume mixture in CCl_4, showed methyl doublets centered at 1.73 (meso) and 1.77 (racemic) ppm.[17] Its isomeric composition was 42% meso and 58% racemic.

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Table I
Conditions for the Polymerizations of Vinyl Bromide (Prefix B) and Vinyl Chloride (Prefix C)

sample desig	polym temp, °C	initiator	initiator concn, mol %	polym time, h	yield, wt %
B1	−78	^{60}Co-γ[a]		18.0	17.8
B2	−45	^{60}Co-γ		6.0	42.5
B3	0	^{60}Co-γ		2.0	47.2
B4	55	AIBN[b]	1.7	21.5	56.0
B5	100	ACHCN[c]	0.0075	2.0	21.8
C1	−78	^{60}Co-γ		16.0	7.0
C2	−45	^{60}Co-γ		3.0	25.0
C3	100	ACHCN	0.015	4.0	77.9

[a] Effective dose rate = 0.34 Mrd/h. [b] Azobis(isobutyronitrile). [c] 1,1′-Azobis(1-cyclohexanenitrile).

Results and Discussion

The details of the polymerizations are given in Table I. A study of the effects of selected additives on the rate of polymerization of vinyl bromide when subjected to cobalt-60 γ radiation was done to determine the nature of the propagating species. This was accomplished by the addition of trace amounts of specific inhibitors for anionic, cationic, and free-radical mechanisms, namely, carbon tetrachloride, acetone, and iodine, respectively.[18] There was a marked inhibition of polymerization only when iodine was present, confirming that the active propagating center was a free radical. The results from radiation initiation may be directly compared therefore with those from the conventional free-radical initiators.

A. Carbon-13 NMR Spectra and Assignments. Figure 1 shows the carbon-13 NMR spectra of poly(vinyl bromide) samples observed under a variety of conditions. The appearance of the spectrum is dependent on solvent, temperature, and polymer molecular weight. Several solvents were tested which, in order of increasing boiling point, were a 1:1 mixture of carbon disulfide with acetone, trimethylene sulfide (thietane), cyclohexanone, thiophenol, and 1,2,4-trichlorobenzene. Chloroform did not dissolve any of our samples, although its use is reported in ref 5. The solubilities of the poly(vinyl bromide) samples paralleled their polymerization temperatures, with the high-temperature samples being the most readily dissolved. Thietane was the only solvent found for samples B1 and B2. Some of the polymer solutions discolored rapidly when heated, owing to facile dehydrobromination of the polymer. No correlation between polymer stability and its preparation temperature or solvent was attempted.

As a prerequisite for stereosequence assignments, the methine or α-carbon resonance (sensitive to "odd-ads") must be distinguished from the methylene or β-carbon resonance (sensitive to "even-ads"). This was accomplished by observing a proton-coupled carbon-13 NMR spectrum and by measuring the carbon-13 spin–lattice relaxation times (T_1 values). In the proton-coupled spectrum, the methine carbon resonance split into a doublet (one bonded proton), and the methylene carbon resonance split into a triplet (two bonded protons). While it was clear that the methine region was downfield from the methylene region, a complete distinction could not be made by this experiment owing to overlap.

The T_1 experiment was conclusive. For example, at 80 °C with B3 dissolved in thietane, the T_1 values were 0.16 s for the methine carbon and 0.09 s for the methylene carbon. Within an experimental error of ±10% these values have the 2:1 ratio predicted by theory. A spectrum was also obtained with the methine resonance nulled by selecting a τ value of 0.11 s in a 180°–τ–90° pulse sequence, thereby revealing the entire methylene region devoid of overlap.

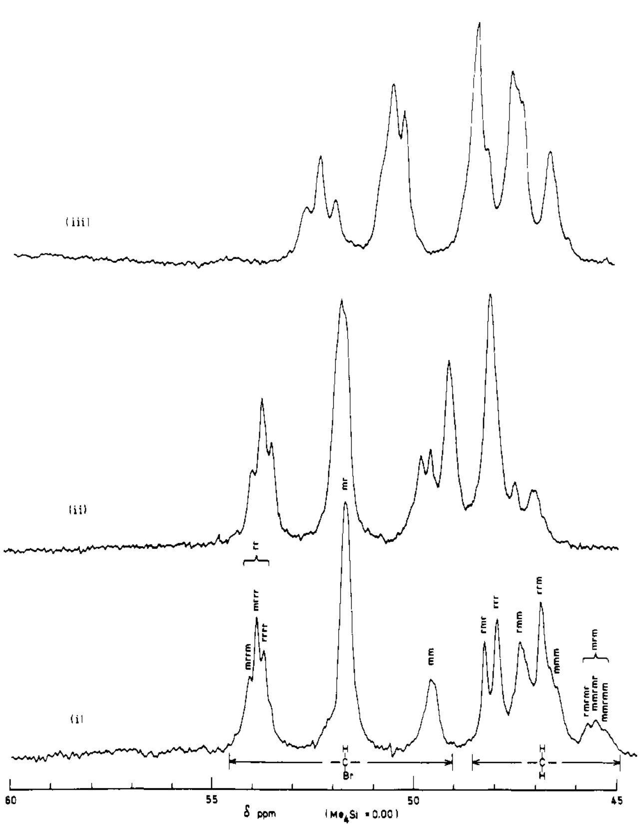

Figure 1. 22.62-MHz carbon-13 NMR spectra of poly(vinyl bromide) samples BA1 (i), B3 (ii), and B4 (iii). Solvents and observation temperatures: (i) carbon disulfide–acetone, 40 °C; (ii) thietane, 80 °C; (iii) 1,2,4-trichlorobenzene, 100 °C. Note the decreased line width for the low molecular weight, aldehyde-modified polymer (i) and the splitting of the heterotactic triad and greater spread of the rr-centered pentads at 100 °C in 1,2,4-trichlorobenzene (iii).

The methine carbon is responsible for the triplet centered at 51.67 ppm in Figure 1 (spectrum i), with a dispersion of 5 ppm induced by triad stereosequential differences. The methylene carbon resonance is more shielded and is a complex, incompletely resolved pattern with a sensitivity to tetrad and longer configurational sequences. The spread is from 45 to 48.5 ppm in spectrum i.

The only solvents which were found to separate the methine from methylene carbon resonances were, in order of increasing effectiveness in reducing the overlap, thiophenol, cyclohexanone, and carbon disulfide–acetone. In other solvents the high-field component of the methine carbon triplet was obscured by the methylene region either partially (in thietane) or completely (in 1,2,4-trichlorobenzene). The appearance of the methine carbon resonance was essentially independent of the observation conditions. It was invariably a well-resolved triplet, with some fine structure from pentad stereosequences. Resolution of this fine structure was improved by raising the observation temperature or by examining samples with a low degree of polymerization.

In contrast, the methylene carbon resonance pattern varied markedly with solvent. The chemical shifts of some stereosequences were more variable than others from one solvent to the next, resulting in a crossing over of individual peaks and an overall scrambling of the resonance pattern. In some solvents, notably cyclohexanone, no structure was discernible, and the methylene resonance was a single broad, asymmetric peak. In other solvents, for example, thiophenol, the pattern was a deceptively simple triplet, which in reality must comprise at least six peaks. The best resolution of hexads in the methylene carbon resonance was achieved with carbon disulfide–acetone as the solvent and the low molecular weight sample BA1 (spectrum i, Figure 1).

Analogous behavior has been observed in the carbon-13 NMR spectra of poly(vinyl chloride),[4] where different solvents have little effect on the methine resonance but a pronounced effect on the methylene resonance. It is clear that specific polymer–solvent interactions are involved, but the mechanism whereby they influence the pattern of stereosequential splittings from one type of carbon, but not the other, is not yet understood.

The stereosequence assignments in the carbon-13 NMR spectrum of poly(vinyl bromide) are given in Figure 1. The most intense peak of the methine carbon triplet (the central one) must necessarily correspond to the heterotactic triad, which incorporates both mr and rm stereosequences. It is also evident that there is a bias in the stereosequence distribution, as one of the homotactic triads is more probable than the other. The difference in peak intensities was most pronounced for sample B1, prepared at −78 °C.

Either meso or racemic placement becomes more likely with decreasing polymerization temperature, and proton NMR spectra showed that racemic dyads are favored, just as in poly(vinyl chloride). In the proton NMR spectra of poly(vinyl bromide) samples, recorded at 28 °C in carbon disulfide–acetone, the methine proton gave a broad resonance at 4.54 ppm and the methylene protons gave a doublet at 2.32 and 2.56 ppm. The low-field component of this doublet decreased in intensity relative to the high-field component with decreasing polymerization temperature. The former component can be associated with the meso or isotactic dyad according to the proton spectrum of 2,4-dibromopentane, where the heterosteric methylene protons of the meso isomer are deshielded with respect to the homosteric methylene protons of the racemic isomer (2.31 and 2.01 ppm, respectively[17]). The above dyad assignments for poly(vinyl bromide) are also in accord with those published by Ramey et al.[6]

In the carbon-13 NMR spectrum of sample B1 the syndiotactic triad resonance therefore must be more intense than the isotactic triad resonance, allowing completion of the triad assignments as indicated in Figure 1. As will be seen in the next section, the triad intensities conform to Bernoullian statistics, so it is a simple matter to calculate pentad intensities, which then give the assignments shown for the pentads centered on the syndiotactic triad.

Model compound carbon-13 data verified these triad assignments. Table II gives the carbon-13 chemical shifts for racemic and meso 2,4-dibromopentanes under a variety of conditions of solvent, temperature, and concentration. The methine carbon in the racemic isomer resonates 2.5 ppm downfield from its counterpart in the meso isomer. Therefore one would expect the mr triad to be 2.5 ppm downfield from the mm triad, as the structural difference involved here is at the dyad level, which is simulated by the model compound isomers. Similarly, one would expect rr to be 2.5 ppm downfield from mr. The model compound thus gives a realistic account not only of the relative ordering of the methine carbon triads in the polymer spectrum but also of their absolute chemical shift dispersion (5 ppm overall). The influence of observation conditions on the methine carbon resonance is also minimal for 2,4-dibromopentane, as for the polymer.

Table II
Carbon-13 Chemical Shifts for a 58:42 Mixture of Racemic and Meso 2,4-Dibromopentanes

observation conditions				$\delta \pm 0.05$[a]		
solvent	concn, % by vol	T, °C	isomer	CH_3	CH_2	CHBr
none	100	35	r	26.40	51.32	49.08
			m	25.34	51.32	46.57
$CDCl_3$	50	35	r	26.44	51.55	49.42
			m	25.37	51.48	46.84
CS_2-acetone (1:1)	50	35	r	26.49	51.67	49.71
			m	25.44	51.75	47.27
1,2,4-TCB[b]-dioxane (4:1)	50	35	r	26.42	51.65	49.19
			m	25.33	51.57	46.66
1,2,4-TCB-dioxane (4:1)	50	100	r	26.46	52.29	48.71
			m	25.50	52.04	46.39
1,2,4-TCB-dioxane (4:1)	5	35	r	26.42	51.86	49.48
			m	25.33	51.74	46.91

[a] $\delta(Me_4Si) = 0.00$. The carbons were assigned from a proton-coupled spectrum, in which the following ${}^1J_{{}^{13}C-{}^1H}$ values were observed: methyl, 128 Hz; methylene, 130 Hz; methine, 154 Hz. [b] Trichlorobenzene.

The model compound data from the methylene carbon, on the other hand, are inadequate for interpretation of the corresponding region of the polymer spectrum, although they gave a good description of the methylene *proton* chemical shifts. This is because three-bond gauche or γ interactions, which are sensitive to conformation and hence stereochemistry, give rise to the dispersion of carbon-13 chemical shifts;[4] the methylene carbon in 2,4-dibromopentane has no γ substitutents. The proton chemical shifts, on the other hand, are determined by their immediate chemical environment to the first approximation. It is hardly surprising therefore that the methylene carbon chemical shifts differ by only a few hundredths of a ppm for the model compound isomers. The solvent effect is minimal, which is not the case for the methylene region in the polymer spectra, but the relative ordering of m and r does change, as is observed for some tetrad peaks in poly(vinyl bromide).

Assignment of the methylene carbon tetrads was attempted only in the instance when all six peaks could be resolved, namely, for the polymer spectrum recorded in carbon disulfide–acetone (spectrum i, Figure 1). The tetrad intensities were calculated on the basis of the triad results and Bernoullian statistics and were matched to the observed spectrum to obtain the assignments. These assignments were also consistent for polymers prepared at several temperatures. The mrm tetrad is split into its three hexads, which were likewise assigned from intensities. Incipient hexad splitting causes the noticeable broadening of the rmm peak. The stereosequence assignments for poly(vinyl bromide) are summarized in Table III.

It is instructive to compare the carbon-13 NMR spectra of poly(vinyl bromide) and poly(vinyl chloride). The comparison is made in Figure 2, where the polymer spectra were recorded under identical conditions. The respective methine carbons differ in absolute chemical shift by nearly 6 ppm (CHBr being more shielded), but the methylene carbons have essentially the same chemical shift. These shifts may by rationalized qualitatively from the halogen-substituent effects, which attribute a smaller α effect to bromine than chlorine (+20 vs. +31 ppm, respectively)

Table III
Carbon-13 Chemical Shifts for the Stereosequences Resolved in Poly(vinyl bromide) When Observed in Carbon Disulfide–Acetone at 40 °C

CHBr			CH$_2$		
stereosequence		δ ± 0.05^a	stereosequence		δ ± 0.05^a
rr	mrrm	54.06		rmr	48.27
	rrrm	53.86		rrr	47.98
	rrrr	53.72		rmm	47.35
rm		51.67		rrm	46.84
mm	mmmm	49.78		mmm	46.46
	rmmm	49.57	mrm	rmrmr	45.70
	rmmr	49.46		rmrmm	45.52
				mmrmm	45.30

^{a} $\delta(\mathrm{Me_4Si}) = 0.00$.

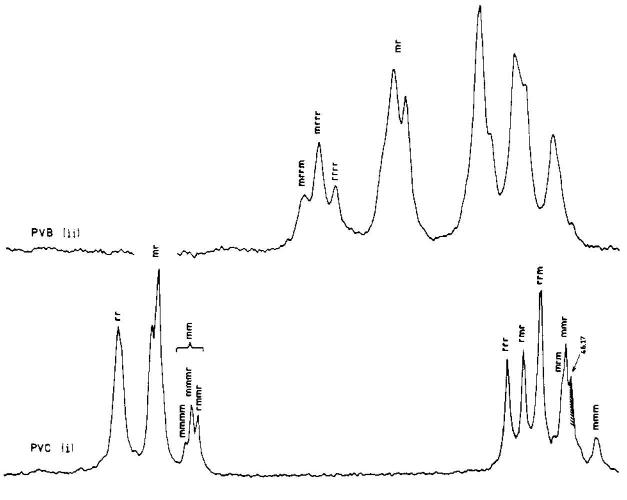

Figure 2. 22.62-MHz carbon-13 NMR spectra of poly(vinyl chloride) sample CA1 (i) and poly(vinyl bromide) sample B4 (ii). Both spectra were obtained in 1,2,4-trichlorobenzene at 100 °C. The hatched peak at 46.17 ppm in spectrum i is assigned to a CH$_2$Cl end group.

but nearly an identical β effect (+10.6 ppm).[19]

Of greater interest is the fact that the methine carbon in poly(vinyl bromide) has twice the chemical shift dispersion of its counterpart in poly(vinyl chloride). This is consistent with the carbon-13 chemical shift data from the 2,4-dihalopentanes. Table III shows that the difference δ(racemic) − δ(meso) for methine carbons is 2.5 ppm for the bromo compound, which is slightly more than twice the corresponding difference reported for the chloro compound.[16,20]

It is difficult to rationalize this twofold greater spread on the simple basis of the magnitude of the γ effects of halogens in 1-haloalkanes, where bromine actually has a smaller effect than chlorine (−3.1 compared to −4.6 ppm).[19] On the other hand, the chemical shift dispersion induced by stereochemical differences is very nearly the same for methylene carbons in either polymer as well as for methyl and methylene carbons in either model compound. This suggests that the major difference must reside in the γ effects of the halogen substituents if the configurational splittings are to be explained by the model based on conformational influences on the proportions of gauche interactions.[4]

B. Configurational Statistics and the Effect of Temperature. With the above configurational sequence assignments for poly(vinyl bromide) it is possible to determine the configurational sequence propagation mechanism. Accurate peak areas must be obtained as a prerequisite, and they were measured by cutting out and weighing and by using a planimeter. The results were indistinguishable.

A potential source of error would be differential nuclear Overhauser enhancements between stereosequences; however, the present data did not reveal any measurable difference.

The unconditional probability of occurrence of any particular stereosequence S is simply its peak area, $A(\mathrm{S})$, divided by the total resonance area of the carbon under observation. This probability is denoted here as $p(\mathrm{S})$, whereas the probability of meso placement for Bernoullian statistics, for example, is denoted P_{m}. The following dyad–triad relations apply irrespective of the propagation statistics:[21]

$$p(\mathrm{m}) = p(\mathrm{mm}) + \tfrac{1}{2}p(\mathrm{rm}) \tag{1}$$

$$p(\mathrm{r}) = \tfrac{1}{2}p(\mathrm{rm}) + p(\mathrm{rr}) \tag{2}$$

$$p(\mathrm{m}) + p(\mathrm{r}) = 1 \tag{3}$$

For Bernoullian statistics

$$p(\mathrm{mm}) = \{P_{\mathrm{m}}\}^2 \tag{4}$$

$$p(\mathrm{mr}) = 2P_{\mathrm{m}}P_{\mathrm{r}} \tag{5}$$

$$p(\mathrm{rr}) = P_{\mathrm{r}}^2 \tag{6}$$

$$P_{\mathrm{m}} + P_{\mathrm{r}} = 1 \tag{7}$$

where the heterotactic triad probabilities refer to the observed values (i.e., rm + mr, since these are indistinguishable). Triad data are necessary and sufficient to *test* for conformance to Bernoullian statistics, but tetrad data are necessary to test first-order Markov statistics if it is found that the former treatment is inappropriate.[21]

The present analysis was based predominantly on the methine carbon triads because of the poor resolution and uncertain assignments of "even-ad" stereosequences from the methylene carbon spectra in solvents other than carbon disulfide–acetone. In most cases all triads from the methine carbon were resolved to the base line, and their unconditional probabilities could be obtained directly. When the mm triad was obscured by the methylene carbon resonance in certain solvents, however, the methine resonance area was obtained by halving the combined methine and methylene areas to allow computation of $p(\mathrm{rr})$, $p(\mathrm{rm})$, and hence $p(\mathrm{mm})$ by difference. For Bernoullian statistics a direct calculation of P_{m} is also possible from the ratio $A(\mathrm{rr})/A(\mathrm{rm})$, which is simply equal to $\{1 - P_{\mathrm{m}}\}/P_{\mathrm{m}}$.

The tacticities of the various poly(vinyl chloride) samples were determined from the methine carbon triads also, which were always well resolved and did not suffer from an overlap problem. The spectra were recorded for solutions in 1,2,4-trichlorobenzene, and the literature assignments[4] (shown in Figure 2) were used.

The stereosequence distribution in all polymers examined in this work adhered to Bernoullian statistics. One test is the equality between $p(\mathrm{r})$, calculated according to eq 2, and P_{r}, calculated according to eq 6. This equality held to within ±0.4% on the average. The P_{m} values are listed in Table IV. The same bias and trend in stereochemical configuration is observed for both polymers in that $p(\mathrm{m})$ is less than 0.5 and racemic placement becomes favored with decreasing temperature (i.e., P_{m} decreases). The differences in activation enthalpies and entropies for meso vs. racemic placement were obtained from a plot of $\ln (P_{\mathrm{m}}/P_{\mathrm{r}})$ against reciprocal temperature, following standard treatment.[8] This plot is shown in Figure 3. The values calculated for $\Delta H_{\mathrm{m}}^{\ddagger} - \Delta H_{\mathrm{r}}^{\ddagger}$ are 1.27 ± 0.03 kJ/mol

Table IV
Probabilities of Meso Dyad Placement with a Bernoullian Propagation Mechanism for Poly(vinyl bromide) and Poly(vinyl chloride)

sample desig	polym temp, °C	$P_m \pm 0.002$
B1	−78	0.386
B2	−45	0.417
B3	0	0.449
B4	55	0.464
B5	100	0.477
BA1[a]	50	0.423
C1	−78	0.396
C2	−45	0.416
E-80[b]	43	0.455
C3	100	0.467
CA1[a]	40	0.398

[a] See Table V for details. [b] This sample was prepared by the Nordforsk Polymer Group and made available through the courtesy of Dr. K. B. Abbås.

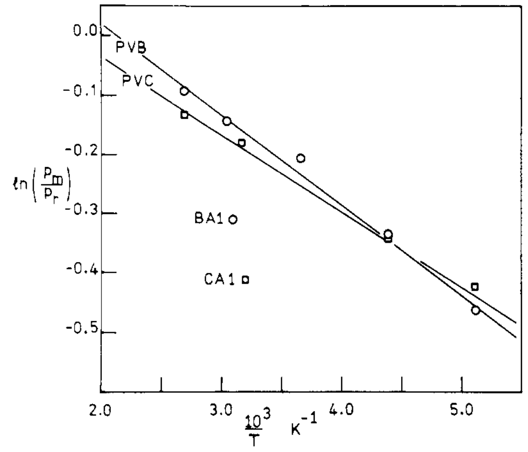

Figure 3. Plot to determine the differences in activation enthalpies and entropies for meso vs. racemic placement in poly(vinyl bromide) (○) and poly(vinyl chloride) (□). $\Delta H_m^‡ - \Delta H_r^‡$ is obtained from the slope and $\Delta S_m^‡ - \Delta S_r^‡$ from the intercept. The points corresponding to the aldehyde-modified polymers are also shown.

for poly(vinyl bromide) and 1.09 ± 0.02 kJ/mol for poly(vinyl chloride). The corresponding $\Delta S_m^‡ - \Delta S_r^‡$ values are 2.72 and 1.90 J/(mol K).

The free energies of activation always favor racemic placement over the temperature range examined here, where the dominant term is the difference in activation enthalpies. However, the difference in activation entropies favors meso placement, so that poly(vinyl bromide) and poly(vinyl chloride) would be perfectly atactic ($p(\mathrm{m}) = 0.5$) if it were possible to prepare the polymers at temperatures of 194 and 300 °C, respectively. The differences in activation enthalpies for the two polymers can be rationalized according to the sizes of the halogen substituents; it is reasonable that the larger bromine substituent accentuates this difference compared to chlorine. The more pronounced steric influence of bromine is also manifested by the relaxation behavior of the polymers. The T_1 values obtained here for poly(vinyl bromide) are half those for poly(vinyl chloride) observed under similar conditions,[22] indicating that backbone motions are constrained more when the α substituent is bromide rather than chlorine.

C. Effect of *n*-Butyraldehyde. Details of the polymerizations in an *n*-butyraldehyde medium are given in Table V. Both aldehyde-modified polymers had a Bernoullian stereosequence distribution, with a significant enhancement in racemic dyad content. The carbon-13 NMR spectrum of the regular methine and methylene carbons in aldehyde-modified poly(vinyl bromide) is shown in Figure 1i, and the poly(vinyl chloride) spectrum is shown in Figure 2i. The P_m values for both polymers are given in Table IV, and the corresponding points are shown on the plot in Figure 3.

Table V
Polymerizations of Vinyl Bromide (Prefix B) and Vinyl Chloride (Prefix C) in an Equimolar Mixture with *n*-Butyraldehyde

sample desig	polym temp, °C	initiator	initiator concn, mol %	polym time, h	yield, wt %
BA1	50	AIBN	0.05	16	0.6
CA1	40	AIBN	0.05	24	26.7

The effect of *n*-butyraldehyde on tacticity is less pronounced for poly(vinyl bromide). The results show that the free energy for racemic placement is further lowered with respect to that for meso placement on addition of *n*-butyraldehyde by 0.20 kJ/mol for poly(vinyl bromide) and by 0.57 kJ/mol for poly(vinyl chloride). It is not possible to determine if this change is reflected in the enthalpy difference or in the entropy difference, or possibly in both, without a variable-temperature study. Rosen et al.[12] have claimed that variation in temperature has no effect on the tacticity of poly(vinyl chloride) produced in *n*-butyraldehyde, but this point bears reinvestigation.

Both aldehyde-modified polymers have a low degree of polymerization, owing to the efficacy of *n*-butyraldehyde as a chain-transfer agent.[12,13,15] Additional studies of the poly(vinyl bromide) sample were precluded by the very small yield of material (Table V), but further work on the poly(vinyl chloride) sample showed that it could be separated with carbon disulfide into soluble (10%) and insoluble (90%) fractions. Furthermore, examination by carbon-13 NMR showed that these fractions had different tacticities, so the fractionation was not on the basis of molecular weight alone. The P_m values were 0.459 for the soluble fraction and 0.392 for the insoluble fraction. The former value is very close to that expected for regular poly(vinyl chloride) prepared at 40 °C, i.e., 0.452, so it appears that there are two independent propagating sites, one of which is not influenced by *n*-butyraldehyde.

The carbon-13 NMR spectra also contained resonances which were assigned to self-condensation products of *n*-butyraldehyde and polymer end groups. Traces of hydrogen halide liberated in the reaction mixture catalyzed the formation of the cyclic trimer of *n*-butyraldehyde, which was responsible for peaks with the following δ values: 14.19, CH_3; 17.27, CH_2; 36.91, CH_2; 101.29, OCHO. These peaks disappeared after heating the polymer solution to 100 °C and after extraction of the polymer with carbon disulfide before observation.

The positions of the end-group resonances supported the initiation and termination mechanisms proposed by Rosen et al.[12] for vinyl chloride:

$$\mathrm{C_3H_7C(O)\cdot} + n(\mathrm{CH_2{=}CHCl}) \rightarrow \mathrm{C_aH_3C_bH_2C_cH_2C_dOC_eH_2CHCl(CH_2CHCl)_{n-1}\cdot}$$

$$\mathrm{C_3H_7CHO} + \sim\!\!\sim\!(\mathrm{CH_2CHCl})_n\cdot \rightarrow \mathrm{C_3H_7C(O)\cdot} + \sim\!\!\sim\!(\mathrm{CH_2CHCl})_{n-1}\mathrm{C_fH_2C_gH_2Cl}$$

The carbon δ values were as follows: a, 13.92; b, 18.02; c, 42.83; d, 198.62; f, multiplet centered at 41.01; g, 46.17. The resonance from carbon e was probably obscured by the more intense repeat-unit resonances. The intensities of these resonances gave number-average degrees of polymerization of about 22 for poly(vinyl bromide) and 40 for poly(vinyl chloride). The smaller value for poly(vinyl bromide) reflects the slower rate of polymerization compared to that of vinyl chloride in the presence of aldehyde (Table V) so that termination is able to compete more effectively with propagation.

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Observation of Stereoirregular Poly(fluoromethylene) by Fluorine-19 Nuclear Magnetic Resonance

R. E. Cais

Bell Laboratories, Murray Hill, New Jersey 07974. *Received January 22, 1980*

ABSTRACT: *cis*-1,2-Difluoroethylene and *trans*-1,2-difluoroethylene were polymerized by ^{60}Co γ radiation at 0 and 37 °C to give poly(fluoromethylene). The appearance of the 84.66-MHz ^{19}F NMR spectra of the polymers was remarkably sensitive to the solvent used for NMR, and stereosequence heptads could be resolved under certain conditions. Assignments were made at the pentad level. The polymers are highly stereoirregular, accounting for their lack of crystallinity. The polymerizations of cis and trans monomers at the same temperature gave polymers with identical tacticities. A reduction of the polymerization temperature enhanced the syndiotactic triad content. The stereosequence distribution at 0 °C is approximated reasonably well by a Bernoullian model with a P(m) value of 0.42.

^{19}F NMR has been a valuable probe of the microstructure of polymers containing fluorine.[1,2] The polymerization of 1,2-difluoroethylene to form poly(fluoromethylene) (PFM) was described in 1965 by Durrell et al.,[3] but since then there has been little interest in the polymer. The only reported NMR study was concerned with its relaxation behavior, and the microstructure was not examined.[4] However, PFM is of considerable interest from the latter point of view, since every backbone carbon is a pseudoasymmetric center and bears the same substituent. To the author's knowledge the only other polymer of this type which has been studied by NMR is poly(hydroxymethylene).[5] The purpose of this paper is to report the high-resolution ^{19}F spectra of PFM.

Experimental Section

cis-1,2-Difluoroethylene (bp −26 °C) and *trans*-1,2-difluoroethylene (bp −53 °C) were obtained from PCR Research Chemicals Inc. The monomers were degassed and fractionally distilled under high vacuum and then sealed in heavy-wall glass ampules (8.02 g, 125 mmol per ampule). Polymerizations were initiated by ^{60}Co γ radiation (effective dose rate = 0.37 Mrd/h) at temperatures of 37 and 0 °C (the rate of polymerization at −78 °C was negligible). The sealed ampules were exposed to γ radiation for 14–16 h, which was sufficient for 100% conversion to polymer at the higher temperature. Conversions at the lower temperature were less and averaged about 25%. An attempt to prepare PFM at 70 °C in heptane with a heterogeneous $TiCl_4$-$Al(C_2H_5)_3$ catalyst system was not successful.

NMR spectra were recorded with a ^{19}F frequency of 84.66 MHz in a variety of solvents on a Bruker WH-90 spectrometer. It was difficult to prepare uniform solutions containing more than about 10% by weight of polymer, owing to a gelation phenomenon in the solvents tested here. A typical spectrum was recorded from 30 000 scans with a 3.4-μs pulse (90° flip angle), 3.0-s repetition rate, 4.0-kHz sweep width, and 8K data points for the real spectrum. Chemical shifts were measured from internal hexafluorobenzene, which was assigned the value of 163 ppm.

Results and Discussion

^{1}H and ^{13}C NMR spectra of PFM did not exhibit any resolved fine structure, owing to the appreciable line broadening from heteronuclear spin coupling between the observed nucleus and ^{19}F, for which we did not have the facilities for broad-band decoupling. The proton resonance was a broad, asymmetric peak centered around 5.2–5.3 ppm. The proton-decoupled ^{13}C resonance was a doublet centered at 87.31 ppm, with a splitting of 163 Hz, corresponding to the $^{1}J_{^{13}\mathrm{C}-^{19}\mathrm{F}}$ value. The dispersion of ^{13}C chemical shift from stereochemical nonequivalence was less

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