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NMR Characterization of the Chemical Microstructure of Vinylidene Halide and Vinyl Halide Copolymers

Rudolf E. Cais,* Janet M. Kometani, and Nita H. Salzman[†]

AT&T Bell Laboratories, Murray Hill, New Jersey 07974. *Received September 12, 1985*

ABSTRACT: Poly(vinylidene halides) having dichloro, dibromo, bromochloro, and fluorochloro geminal substituents have been examined by NMR spectroscopy, and it has been determined that the polymers with asymmetrical substitution are atactic. A series of vinylidene bromide–vinylidene chloride copolymers was prepared and analyzed by 500-MHz proton and 125.8-MHz carbon-13 NMR, which resolved monomer sequence tetrad structure. The sequence distribution conformed to a first-order Markov model with $r_B = 0.9$ and $r_C = 0.8$. Vinyl bromide–vinyl chloride copolymers proved more difficult to examine by NMR, owing to complication by tacticity effects. The analysis was rendered tractable by reductively debrominating the copolymers to the structural equivalent of ethylene–vinyl bromide–vinyl chloride terpolymers. Bromine could not be completely eliminated without partial reaction of chlorine. The resulting monomer sequence distribution was described by the reactivity ratios $r_B = 1.0$ and $r_C = 0.8$, in good accord with literature values and the *Q–e* scheme. Bromine and chlorine substituents have very similar effects on monomer and radical reactivities in the above copolymerizations.

Introduction

High-resolution NMR spectroscopy is the most useful technique for analysis of the chemical microstructure of polymers.[1,2] It is used routinely to identify and measure isomerism involving stereoconfigurational relationships (tacticity) in homopolymers and monomer sequence distributions in copolymers.[3] However, in many cases the analysis of copolymer NMR spectra is complicated by the existence of both forms of isomerism, so that the assignment of resonance fine structure to either tacticity or monomer sequence effects can be difficult.

This problem does not arise with vinylidene bromide–vinylidene chloride (VB_2–VC_2) copolymers, owing to the absence of asymmetric carbons. Therefore these copolymers provide a model system for the analysis of monomer sequence isomerism by NMR spectroscopy. In contrast, the NMR analysis of vinyl bromide–vinyl chloride (VB–VC) copolymers is not nearly as straightforward, owing to the interleaving of multiplet patterns caused by both tacticity and monomer sequence differences. We adopt a novel approach to analyze the latter system by quantitative debromination of the copolymers to the structural equivalent of ethylene–vinyl chloride (E–VC) copolymers, which are more amenable to sequence determination by NMR.

This work continues our previous studies of poly(vinyl halides) (–(CH_2CHX)–), where X is fluorine,[4] chlorine,[5] or bromine.[6] In addition we examine the unsymmetrical poly(vinylidene halides) –(CH_2CXY)– in order to observe halogen substituent effects on chemical shifts in polymer NMR spectra.

Knowledge of the monomer sequence distributions in the above systems provides more detailed information about the propagation statistics than simple monomer–copolymer composition data.[1] Thus we are able to test whether the first-order Markov copolymerization model with two reactivity ratios gives a realistic description of these copolymerizations. We are then able to compare the relative effects of bromine and chlorine substituents on monomer and radical reactivities from the appropriate reactivity ratios.

Experimental Procedures

Monomers. Vinylidene bromide (VB_2) was prepared by the dehydrobromination with ethanolic KOH of 1,1,2-tribromoethane, which was obtained by the addition of bromine to vinyl bromide. Vinylidene bromochloride (VBC) was prepared in a like manner from 1,2-dibromo-1-chloroethane.[7] Vinylidene chloride (VC_2) was supplied by Polysciences and purified by washing with 5% aqueous KOH and then water, followed by drying over molecular sieves. Vinylidene chlorofluoride (VCF) was obtained from PCR Research Chemicals. Vinyl bromide (VB) and vinyl chloride (VC) were commercial products from Matheson. The above monomers were degassed and distilled under high vacuum immediately prior to use.

Polymerizations. All polymerizations were initiated by free radicals, generated either by the thermal decomposition of 0.1 mol % azobis(isobutyronitrile) (AIBN) or by exposure to cobalt-60 γ radiation (dose rate 0.23 Mrad/h) for temperatures at or below 0 °C. The monomers were measured by their gas pressure in a calibrated manifold and sealed under vacuum in glass ampules without added solvents or diluents. In addition, the VB_2:VC_2 molar ratio in the initial and final monomer feed mixtures could be measured simply from proton NMR spectra by comparing the areas of the methylene proton resonances at 6.2 ppm (VB_2) and 5.5 ppm (VC_2). Copolymerizations took place at 60 °C, and conversions were kept low (generally less than 10%) to minimize drift in feed compositions. We also attempted to prepare vinylidene chloride–vinylidene fluoride copolymers, but obtained a poor yield of essentially the homopolymer PVC_2. The copolymers were recovered in methanol, after residual monomer had been stripped off under vacuum, and dried in a vacuum oven.

Reductive Dehalogenations. The VB–VC copolymers were reacted with tri-*n*-butyl-tin hydride to selectively replace bromine with hydrogen. The standard procedure using AIBN as the initiator[8] was modified by carrying out the reduction at 0 °C with ultraviolet light. Thus removal of bromine was essentially complete after only 3 h, and thermal side reactions were minimized. The solvent was tetrahydrofuran, and a 20% excess (based on moles of bromine) of tri-*n*-butyl-tin hydride was used. The radiation source was a 100-W Hanovia medium-pressure mercury vapor lamp contained within a quartz jacket which was immersed in the polymer solution.

NMR Spectroscopy. Proton and ^{13}C NMR spectra were obtained by using Varian XL-200 (200 and 50.31 MHz, respectively) and JEOL GX-500 (500 and 125.8 MHz, respectively) spectrometers. Fluorine-decoupled carbon-13 NMR spectra were recorded on a modified Bruker WH-90 spectrometer.[9] All chemical shifts are referenced to internal tetramethylsilane.

The VB_2–VC_2 copolymers had limited solubility, and thietane was the solvent of choice.[10] The observation temperature was 65–80 °C, although copolymers with more than 50 mol % VB_2 dehydrobrominated very rapidly under these conditions and could not be studied. Lower temperatures caused precipitation of the copolymers. The VB–VC copolymers were more soluble and stable and could be observed in 1,2,4-trichlorobenzene at 100 °C. Carbon types (methylene, methine, and quaternary) were identified in

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[†] Present address: NYU Medical Center, New York, NY 10016.

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Table I
Chemical Shifts and Full Line Widths at Half-Height (in Hz) for the Carbon-13 Resonances from Vinylidene Halide Homopolymers[a]

	carbon type			
	quaternary		methylene	
polymer	δ	$\Delta\nu_{1/2}$	δ	$\Delta\nu_{1/2}$
PVF_2	120.9	6	44.9	12
PVC_2	85.6	5	61.8	12
PVB_2	60.0	6	65.8	12
PVFC	108.8	6	54.1	12
PVBC	74.0	8	63.5	18

[a] Observed at 50.31 MHz. The solvents and observation temperatures are as follows: PVF_2, dimethylformamide, 90 °C; PVC_2 and PVBC, hexamethylphosphoramide, 25 °C; PVB_2, thietane, 80 °C; and PVFC, acetone, 35 °C.

spectra edited by the DEPT experiment.[11] Other relevant details are given in the subsequent discussion and the appropriate figure captions.

Monomer Sequence Analysis. Reactivity ratios were computed from composition data by using the Kelen–Tüdős procedure[12] and used as input for a computer program that generated monomer sequence distribution curves for diads, triads, and tetrads. These curves provide an independent test of the validity of the reactivity ratios and copolymerization model. The methylene proton and carbon-13 spectra were then simulated at the tetrad level by a computer program that generated Lorentzian lines and compared with the observed spectra as a final check on the above procedure. The input data consisted of monomer feed ratio, reactivity ratios, tetrad chemical shifts, and line widths.

Results and Discussion

1. Vinylidene Halide Homopolymers. The homopolymers from the unsymmetrical vinylidene halides $CH_2{=}CXY$ contain pseudoasymmetric centers and therefore have the potential for stereoconfigurational isomerism. In fact, both PVCF and PVBC as prepared here are atactic polymers. The fluorine-19 NMR spectrum of PVCF shows three well-resolved lines corresponding to isotactic (*mm*), heterotactic (*mr*), and syndiotactic (*rr*) triads, as reported in our previous work.[4] Some pentad fine structure is partially resolved. The triad proportions are insensitive to polymerization temperature over the range −80 to +45 °C and conform to a perfectly Bernoullian distribution with $p(m) = 0.5$. This is in contrast to the usual situation for vinyl polymers where racemic diad formation becomes more probable at lower temperature.[13]

The methylene protons in PVBC give five lines centered at 4.4 ppm (polymer dissolved in hexamethylphosphoramide-d_{18} at 45 °C), which consist of a singlet plus a quartet. Methylene protons in the racemic diad are homosteric (singlet), and those in the meso diad are heterosteric (quartet).[13] These peaks are not resolved well enough to obtain the meso-to-racemic diad ratio, but it is clear that the polymer is atactic with no distinct stereochemical bias.

Surprisingly, carbon-13 NMR is totally insensitive to stereochemical irregularity in both PVCF and PVBC. For example, the methylene and quaternary carbons have line widths comparable to those observed for the corresponding carbons in the symmetrical homopolymers PVF_2, PVC_2, and PVB_2, as indicated in Table I. Thus the stereoirregularity in PVCF and PVBC causes no significant dispersion of carbon-13 chemical shift.

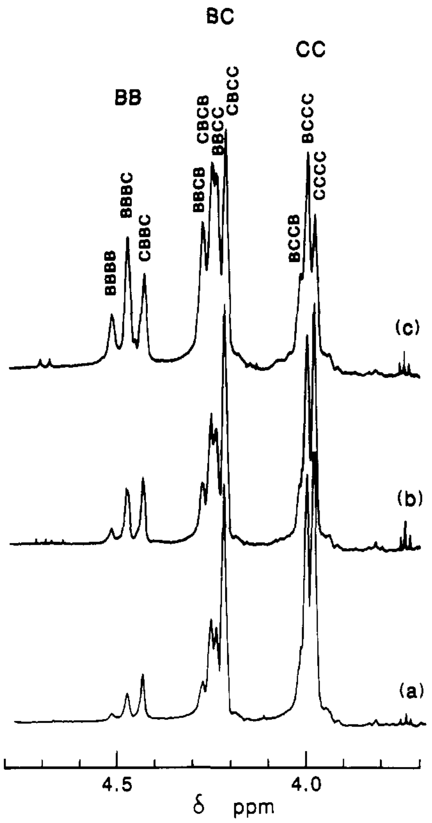

Figure 1. 500-MHz NMR spectra of the methylene protons in vinylidene bromide–vinylidene chloride (VB_2–VC_2) copolymers observed at 65 °C in thietane. The mole fractions of VB_2 in the copolymers are (a) 0.24, (b) 0.32, and (c) 0.42. The tetrad monomer sequence fine structure was assigned on the basis of relative peak intensities. All 16 tetrads are not designated explicitly, since each of the unsymmetrical sequences BBBC, BBCB, CBCB, BBCC, CBCC, and BCCC is observationally equivalent to its corresponding reverse sequence, namely CBBB, BCBB, BCBC, CCBB, CCBC, and CCCB, respectively.

Table II
Methylene Proton Chemical Shifts in Vinylidene Bromide–Vinylidene Chloride (VB_2–VC_2) Copolymers[a]

tetrad sequence	δ	tetrad sequence	δ
BBBB	4.52	BBCC + CCBB	4.24
BBBC + CBBB	4.48	CBCC + CCBC	4.22
CBBC	4.43	BCCB	4.02
BBCB + BCBB	4.28	BCCC + CCCB	4.00
CBCB + BCBC	4.25	CCCC	3.98

[a] Observed at 65 °C in thietane.

2. Vinylidene Halide Copolymers. A series of vinylidene bromide–vinylidene chloride (VB_2–VC_2) copolymers was made at 60 °C with initial monomer feed compositions having 9.8, 20, 21, 30, 40, and 50 mol % VB_2. The 500-MHz proton NMR spectra for several compositions are shown in Figure 1. The methylene proton resonances are split by monomer sequence diads, with peaks at 4.0, 4.25, and 4.5 ppm from CC, BC, and BB sequences, respectively (B = VB_2, C = VC_2). There is complete sensitivity to tetrad sequences, with resolved fine structure appearing for all 10 tetrad sequences. These have been assigned in Figure 1 by examining the range of copolymer compositions and following the change in relative peak intensities with overall composition and by noting the methylene proton chemical shifts in the homopolymers PVB_2 and PVC_2. These shifts are summarized in Table II.

The areas of the NMR peaks were measured and converted to the unconditional probabilities of all tetrad sequences, from which the unconditional probabilities of the diad sequences p(BB), p(BC), and p(CC) may be derived. The following general equations are applicable.

$$p(\mathrm{BB}) + p(\mathrm{BC}) + p(\mathrm{CB}) + p(\mathrm{CC}) = 1$$

$$p(\mathrm{BB}) + p(\mathrm{BC}) = p(\mathrm{B})$$

$$p(\mathrm{CB}) + p(\mathrm{CC}) = p(\mathrm{C})$$

$$p(\mathrm{BB}) = p(\mathrm{BBBB}) + p(\mathrm{BBBC}) + p(\mathrm{BBCB}) + p(\mathrm{BBCC})$$

$$p(\mathrm{BC}) = p(\mathrm{CB}) = p(\mathrm{BCBB}) + p(\mathrm{BCBC}) + p(\mathrm{BCCB}) + p(\mathrm{BCCC})$$

$$p(\mathrm{CC}) = p(\mathrm{CCCC}) + p(\mathrm{CCCB}) + p(\mathrm{CCBC}) + p(\mathrm{CCBB})$$

The probabilities of unsymmetrical tetrad sequences conform to the principle of equivalence upon sequence reversibility, e.g., $p(\mathrm{BBBC}) = p(\mathrm{CBBB})$, $p(\mathrm{BBCB}) = p(\mathrm{BCBB})$, $p(\mathrm{BBCC}) = p(\mathrm{CCBB})$, $p(\mathrm{BCBC}) = p(\mathrm{CBCB})$, etc. An unsymmetrical sequence cannot be observationally distinguish from its reverse by NMR, so both must be summed to correspond to the total integrated peak area. Only one of the unsymmetrical sequences will be designated explicitly in the figures for clarity.

The macroscopic copolymer composition may be expressed as the mole fraction of B units, which is equal to $p(\mathrm{B})$, and can be derived by proton NMR using the appropriate equations above to reduce the observed probabilities of tetrads to diads and finally monads. NMR studies of copolymers are used routinely in this manner to determine overall or macroscopic composition, but the technique has broader scope in its ability to measure sequence distributions, which give a more detailed test of copolymerization models.[1]

Figure 2 shows the 125.8-MHz carbon-13 NMR spectrum for the copolymer with 24 mol % $\mathrm{VB_2}$, which has similar sequence detail to the proton spectra. There are three groups of resonances from the methylene carbon ($\mathrm{CH_2}$) and the two quaternary carbons ($\mathrm{CBr_2}$, $\mathrm{CCl_2}$), centered at 64.4, 58.3, and 86.5 ppm, respectively. These carbon types were assigned by noting the chemical shifts observed for the respective homopolymers (Table I) and by the DEPT experiment.[11] Both quaternary carbon resonances have three components from monomer sequence triads with the following δ values: ($\mathrm{CCl_2}$) BCB, 87.7; BCC, 86.5; CCC, 85.3 ppm; ($\mathrm{CBr_2}$) BBB, 60.0; BBC, 58.3; CBC, 56.5 ppm. At 125.8 MHz pentad fine structure, which cannot be observed at 50.31 MHz, is just resolved on the quaternary carbon resonances. The methylene carbon signal is split into three main peaks, which are assigned to diads: ($\mathrm{CH_2}$) BB, 65.5; BC, 64.4; CC, 63.3 ppm. Nine of the possible ten tetrads are resolved, with overlap of the CBCB and BBCC sequences. These are shown in more detail in Figure 3, and a listing of the corresponding chemical shifts is given in Table III.

The methylene carbons have a T_1 value of 0.33 s and a maximum NOE (at 4.7-T field strength), which ensure quantitative results with the pulse interval of 3.0 s that was used for the XL-200 data. The areas of the methylene carbon resonances therefore give undistorted values for the unconditional probabilities of monomer sequence tetrads, which can be used to derive reactivity ratios as shown below. The tetrad sequence probabilities derived from the carbon-13 NMR spectra are in good agreement with the corresponding values measured from methylene proton NMR spectra (vide supra). The nonprotonated $\mathrm{CBr_2}$ and $\mathrm{CCl_2}$ carbons are more liable to intensity distortions, owing to their long relaxation times, and were not used for quantitative sequence measurements.

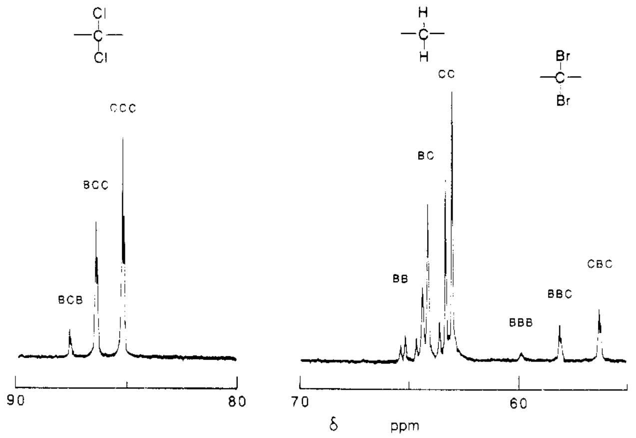

Figure 2. 125.8-MHz carbon-13 NMR spectrum from a $\mathrm{VB_2}$–$\mathrm{VC_2}$ copolymer containing 24 mol % $\mathrm{VB_2}$ and observed at 80 °C in thietane. The carbon types were assigned from the model polymers (Table I) and the DEPT experiment.[11]

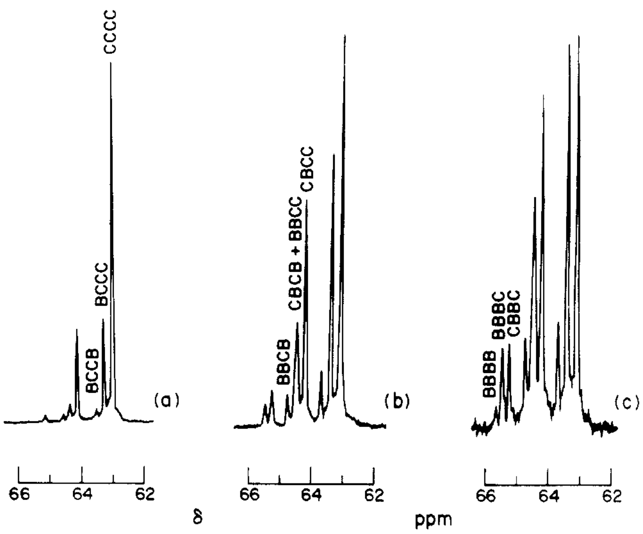

Figure 3. 125.8-MHz carbon-13 resonances from the methylene carbons in $\mathrm{VB_2}$–$\mathrm{VC_2}$ copolymers containing the following mole fractions of $\mathrm{VB_2}$: (a) 0.11; (b) 0.24; (c) 0.32. The tetrad monomer sequence fine structure was assigned on the basis of relative peak intensities.

Table III
Methylene Carbon-13 Chemical Shifts in Vinylidene Bromide–Vinylidene Chloride ($\mathrm{VB_2}$–$\mathrm{VC_2}$) Copolymers[a]

tetrad sequence	δ	tetrad sequence	δ
BBBB	65.81	BBCC + CCBB	64.46
BBBC + CBBB	65.51	CBCC + CCBC	64.14
CBBC	65.27	BCCB	63.74
BBCB + BCBB	64.78	BCCC + CCCB	63.34
CBCB + BCBC	64.46	CCCC	63.04

[a] Observed at 80 °C in thietane.

Diad probabilities are sufficient to solve for the two reactivity ratios r_B and r_C by using the following equations and assuming that the first-order Markov model is appropriate.[1]

$$p(\mathrm{BB}) = p(\mathrm{B})P(\mathrm{B/B})$$

$$p(\mathrm{CC}) = p(\mathrm{C})P(\mathrm{C/C})$$

$$P(\mathrm{B/B}) = r_B f_B/(r_B f_B + f_C)$$

$$P(\mathrm{C/C}) = r_C f_C/(r_C f_C + f_B)$$

The conditional probability of adding monomer Y to chain terminus X is designated by $P(\mathrm{X/Y})$. The mole fraction

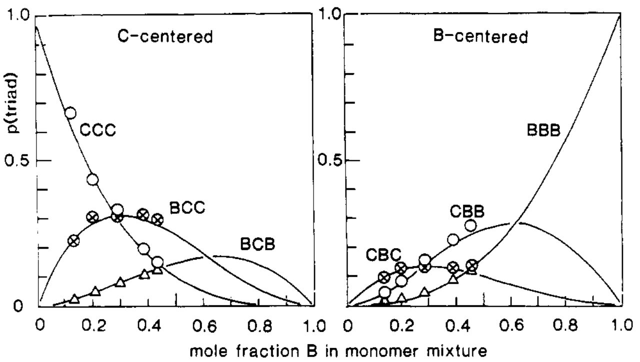

Figure 4. Comparison of the observed triad monomer sequence data with the predicted sequence distribution curves calculated for a first-order Markov copolymerization model with $r_B = 0.9$ and $r_C = 0.8$.

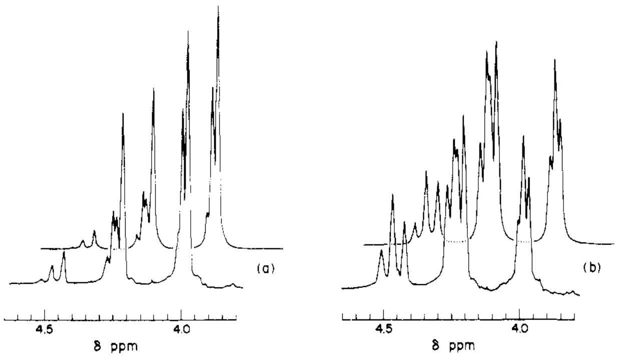

Figure 5. Comparison of the observed 500-MHz methylene proton spectra (bottom) for VB_2–VC_2 copolymers having (a) 24 and (b) 42 mol % VB_2 with simulated spectra (top) generated with $r_B = 0.9$ and $r_C = 0.8$ and (a) $f_B = 0.2$ and (b) $f_B = 0.39$, using the tetrad assignments of Figure 1. Lorentzian line shapes have been assumed.

of monomer in the mixture is given by f_B and f_C.

The above equations show that measurement of diad probabilities for a single copolymer is sufficient to give reactivity ratios. This method is simpler than the traditional approach of determining macroscopic copolymer compositions over a wide range of monomer feed ratios and applying some form of linear regression analysis. However, there was variation from sample to sample in the values for r_B and r_C calculated from the set of diad probabilities obtained by the above NMR analysis due to experimental uncertainties.

Accordingly the values were refined by using the Kelen–Tüdös analysis of monomer–copolymer composition data and subsequent matching of computed sequence distribution curves and methylene tetrad spectra to the observed results. The agreement for triad data is shown in Figure 4, where we are limited to the range of monomer feed compositions less than 50 mol % VB_2 owing to the stability and solubility problems noted above. Figures 5 and 6 compare the computed methylene proton and carbon-13 line shapes with the observed spectra for two copolymer compositions.

The best values of the reactivity ratios in accord with the above procedures are $r_B = 0.9 \pm 0.1$ and $r_C = 0.8 \pm 0.1$. Only r_B differs significantly in the corresponding values of 1.9 and 1.0 reported by Wichterle and Zelinka.[14] We do not find any significant deviation from the terminal or first-order Markov copolymerization model over the range of compositions studied. The reactivity ratio values are close to unity within experimental error, so that the VB_2–VC_2 copolymerization closely approximates ideal Bernoullian behavior for which $r_B = r_C = 1$.

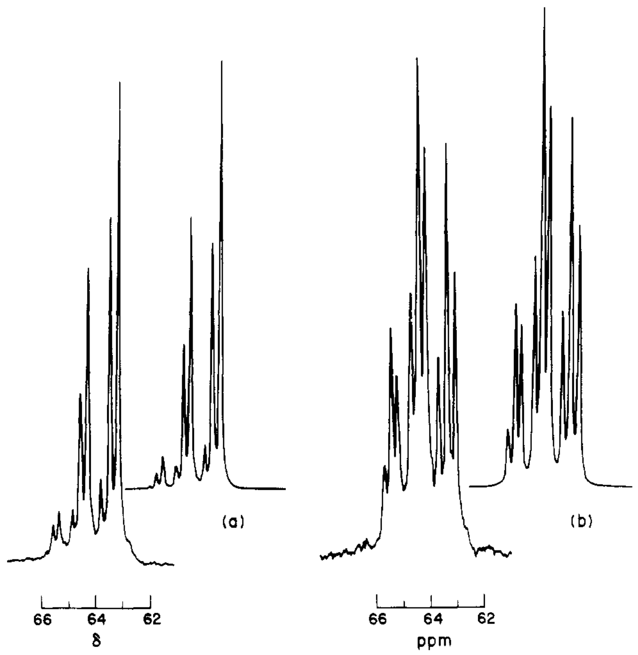

Figure 6. Comparison of the observed 50.31-MHz methylene carbon-13 NMR spectra (bottom) for VB_2–VC_2 copolymers having (a) 24 and (b) 42 mol % VB_2 with simulated spectra (top) generated with $r_B = 0.9$ and $r_C = 0.8$ and (a) $f_B = 0.2$ and (b) $f_B = 0.39$, using the tetrad assignments of Figure 3. Lorentzian line shapes have been assumed.

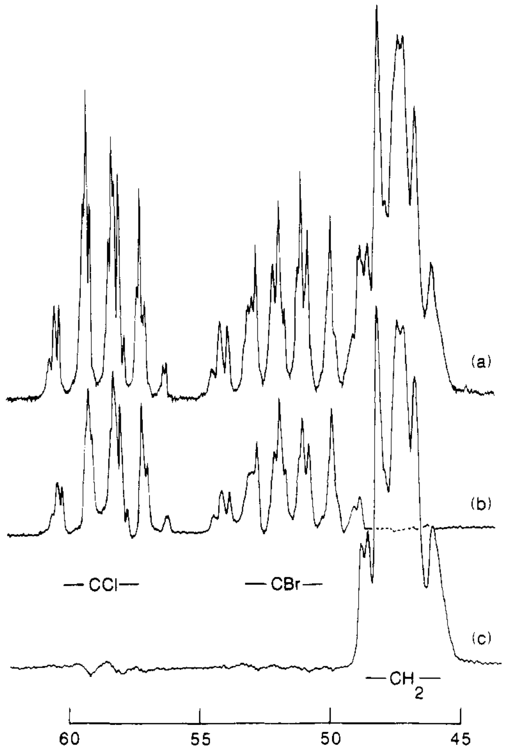

Figure 7. 125.8-MHz carbon-13 NMR spectrum of a vinyl bromide–vinyl chloride (VB–VC) copolymer containing 51 mol % VB observed at 50 °C in tetrahydrofuran-d_8 (a) and the edited spectra obtained at 50.31 MHz by using the DEPT experiment showing the methine carbons (b) and the methylene carbons (c).

3. VB–VC Copolymers. Three VB–VC copolymers were made at 0 °C by using cobalt-60 γ radiation to initiate the copolymerization. The VB/VC monomer feed ratios were 25/75, 50/50, and 75/25 (by moles). The overall copolymer compositions were 29/71, 51/49, and 78/22 VB/VC, respectively, as determined by comparing the

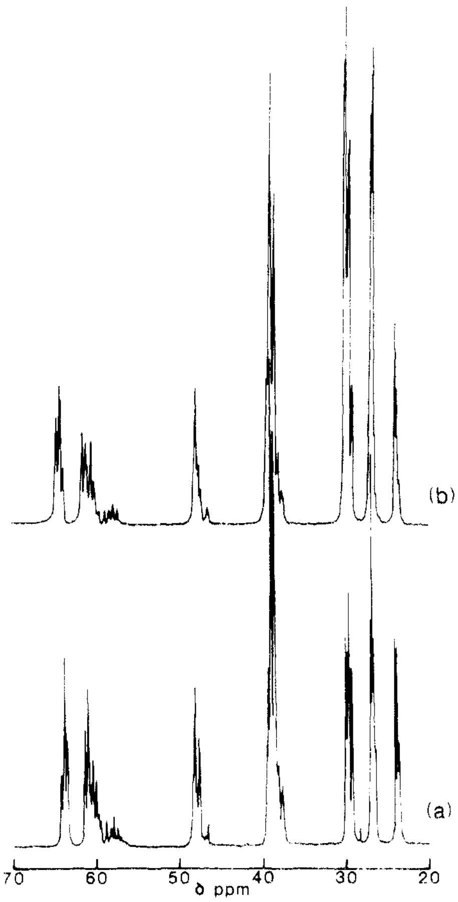

Figure 8. 50.31-MHz carbon-13 NMR spectra of (a) poly(vinyl chloride) with 51 mol % chlorine removed by tri-*n*-butyl-tin hydride and (b) a 51/49 VB/VC copolymer reduced to 39 mol % residual halogen. Both samples observed at 100 °C in 1,2,4-trichlorobenzene.

bromo and chloro methine carbon-13 resonances areas (vide infra). However, a more detailed sequence analysis was not possible. The reactivity ratios $r_B = 1.0 \pm 0.2$ and $r_C = 0.8 \pm 0.2$ were derived by the Kelen–Tüdös procedure[12] using these composition data and checked according to the sequence distribution analysis described later.

Figure 7 shows the 125.8-MHz carbon-13 NMR spectrum of the 51/49 VB/VC copolymer and the edited subspectra obtained by a 50.31-MHz DEPT experiment. It is clear there is some overlap from methine and methylene carbons. The separate methine carbon regions (CHBr, CHCl) were integrated to obtain overall composition as noted above, but further analysis is complicated by the combination of stereosequence and monomer sequence isomerism, especially since both have comparable effects on the extent of chemical shift dispersion.

For example, the methine carbon resonances in the homopolymers PVB and PVC are split into three components due to triad stereosequences, with additional pentad fine structure.[5] These resonances are not dispersed significantly by monomer sequence structure in the copolymers. Figure 7 shows that the methine resonances now have five components in the copolymer spectra, with triplet fine structure superimposed. In contrast, the methylene carbon resonance remains sensitive to stereochemical tetrads, with no apparent additional fine structure from monomer sequences.

Thus at least 30 lines require consideration in the 125.8-MHz methine carbon spectra, but there is no present basis for distinguishing monomer sequence effects from stereosequence effects. For this reason we adopted the strategy of chemically converting the copolymer into a new structure that can be sequenced by NMR while still preserving the original monomer sequence distribution.

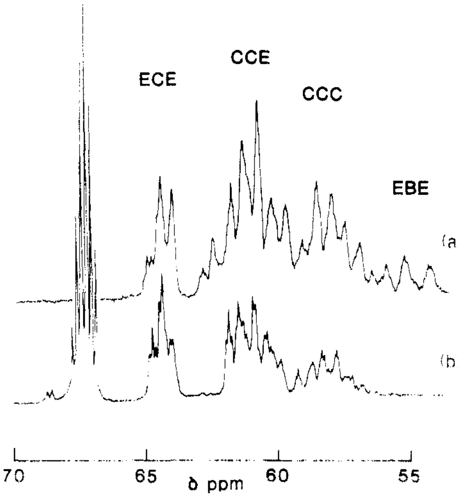

Figure 9. Carbon-13 NMR spectra of the methine region in the 51/49 VB/VC copolymer after removal of (a) 50 mol % halogen and (b) 55 mol % halogen. Spectrum a was obtained at 50.3 MHz, and spectrum b was obtained at 125.8 MHz. Both spectra were recorded at 100 °C with 4:1 by volume 1,2,4-trichlorobenzene: dioxane-d_8 solvent mixture. Ethylene unit = E, vinyl chloride unit = C, and vinyl bromide unit = B. The multiplet at 67 ppm is due to dioxane-d_8.

Accordingly the carbon-13 NMR spectrum shown in Figure 8 results after the 51/49 VB/VC copolymer is treated with tri-*n*-butyl-tin hydride. This figure also shows the carbon-13 NMR spectrum from PVC that has had 51 mol % of its chlorine removed with the tin hydride reagent. Clearly these polymers contain identical structural environments with somewhat different proportions. They are both structurally equivalent to ethylene–vinyl chloride (E–C) copolymers which can be analyzed for monomer sequence distribution by carbon-13 NMR.[15] If the reduction has been completely selective by removing just bromine, the final copolymer will map the distribution of vinyl bromide units (B) with ethylene units (E), and the vinyl chloride units (C) should remain unaffected. As we shall see, this is not entirely the case because all bromine cannot be removed completely under our experimental conditions without removing some chlorine as well.

Figure 9 shows the methine carbon-13 resonances from the 51/49 VB/VC copolymer after removal of 50 and 55 mol % halogen. These resonances are split according to the monomer sequence triads ECE, CCE, and CCC in order of increasing field.[15] Residual vinyl bromide sequences are identified by the EBE resonances after removal of 50 mol % halogen and only vanish after 55% reduction, which must necessitate the removal of some chlorine as well. Prior to this stage the material is an E–B–C terpolymer.

The methylene carbon resonances shown in Figure 10 confirm the above finding. These resonances are split primarily according to the sequence diads CC, EC, and EE from low to high field. Triad monomer sequence fine structure is well resolved in the EE region, where the sequences EEE, BEE, CEE, BEC, and CEC can be distinguished as shown. These assignments were made in accord with published data on E–C[15] and E–B[6] copolymers. Traces of unreacted VB units can be detected in this region as BEE and BEC sequences (spectrum a) after removal of 50 mol % halogen (46% B + 4% C). BEB sequences were not observed. After removal of 61 mol % halogen (51% B + 10% C) there is no residual bromine (spectrum

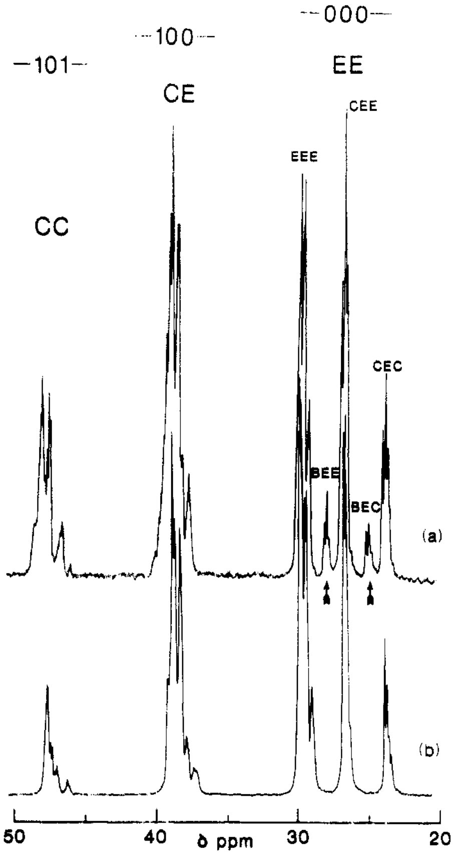

Figure 10. 50.31-MHz carbon-13 NMR spectra from the methylene carbons in the 51/49 VB/VC copolymer after removal of (a) 50 % halogen and (b) 61 mol % halogen. The spectra were recorded at 100 °C with 4:1 by volume 1,2,4-trichlorobenzene: dioxane-d_8 solvent mixture. The carbon types are designated by 1 for methine and 0 for methylene. Residual VB units appear as BEE and BEC sequences (arrows).

b), and the reduced material is a binary E–C copolymer.

We anticipated from the published rate constants for reduction of simple monohaloalkanes that there would be negligible chlorine loss before complete removal of bromine. The curves in Figure 11a show this assuming pseudo-first-order kinetics with a k_B/k_C rate constant of 11 118/1, as reported for cyclohexyl halides by Carlsson and Ingold.[16] In reality the relative rates of halogen removal are better described by a k_B/k_C reactivity ratio around 20, which gives the curves in Figure 11b. Even so, the individual rate constants will depend on monomer and stereosequence environments, so it is highly approximate to assign single values to k_B and k_C. It is not our purpose here to examine these kinetic aspects further.

The reduction technique still enabled the determination of monomer sequence structure in VB–VC copolymers in spite of the incomplete selectivity. This is because the residual B-centered sequences are exclusively EBE (evidently VB units flanked by E are least reactive), and these can be distinguished clearly by carbon-13 NMR as can be BEE and BEC which are the only other triad sequences remaining that incorporate the B unit.

The three copolymers were reductively debrominated to the point where the maximum amount of bromine was removed without reaction of chlorine and examined by carbon-13 NMR as described above. However, it is not quite straightforward to relate the carbon sequence types directly observed by NMR to the various monomer sequence types because an observed sequence is defined by an odd number of carbons, whereas a monomer sequence is defined by an even number of carbons. For example, the methylene carbon resonances shown in Figure 10 are separated into three distinct regions from low to high field according to whether the observed carbon has two, one, or zero β-halogen substituents, respectively. The appropriate carbon sequence types are 101, 100, and 000 (1 = methine, 0 = methylene), and it is their probabilities $P_{obsd}(101)$, $P_{obsd}(100)$, and $P_{obsd}(000)$ that are observed directly by NMR. However, these sequences are part of four-carbon sequences defined by monomer-sequence diads.

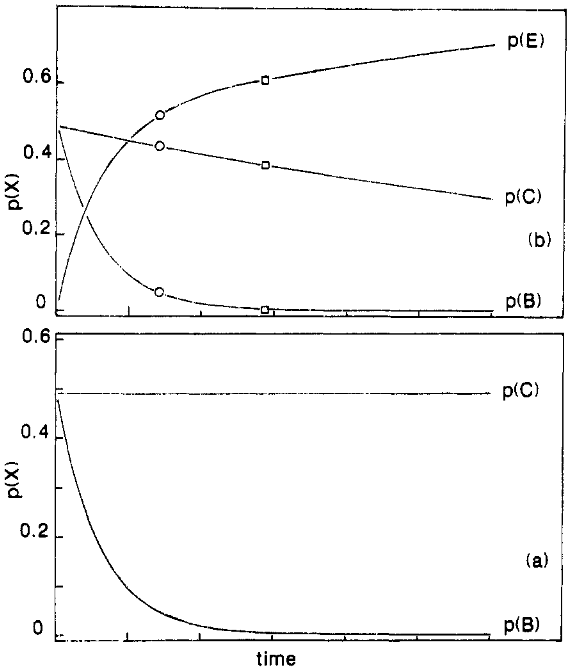

Figure 11. Plot of the probabilities of observing vinyl bromide (B), vinyl chloride (C), and ethylene (E) units vs. the extent of reduction of a 51/49 VB/VC copolymer, assuming first-order kinetics and k_B/k_C rate constant ratios of (a) 11 118 (ref 16) and (b) 20. The experimental points correspond to (a) 51% halogen removal (circles) and (b) 61% halogen removal (squares).

Ultimately, we require monomer sequence probabilities for testing the copolymerization model. We used our procedure reported for the analysis of poly(vinylidene fluoride)[17] to relate carbon sequence types to monomer sequence types, as this method gives a general approach to dealing with the odd–even problem above. Thus the following relationships can be established:

$$P_{obsd}(101) = \tfrac{1}{2}p(VV)$$

$$P_{obsd}(100 + 001) = \tfrac{1}{2}p(VE) + \tfrac{1}{2}p(EV)$$

$$P_{obsd}(000) = p(EE) + \tfrac{1}{2}p(EV)$$

Here $p(VV)$ is the unconditional probability of formation of the VV monomer sequence diad, where V can be either B or C. Since bromine and chlorine have virtually the same β-substituent effect on carbon-13 chemical shifts,[18] it is not possible to distinguish BB, BC, and CC diads in our spectra where stereochemical effects broaden the resonances significantly. Likewise, methylene carbon resonances from BE and CE diads overlap.

Fortunately, complete monomer sequence triad information can be deduced from the methine carbon resonances (Figure 9) and the EE–methylene carbon fine structure (Figure 10). The 000 region is further split according to the carbon sequences 00000, 10000, and 10001 from low to high field, reflecting the increasing shielding influence imposed by zero, one, and two γ-halogen substituents, respectively. Bromine has a smaller γ effect than

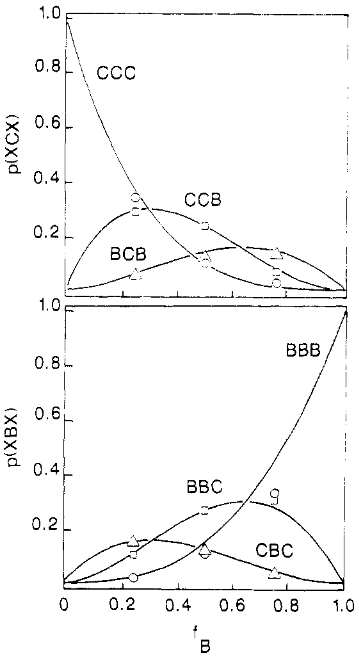

Figure 12. Triad monomer sequence distributions predicted by the first-order Markov copolymerization model with $r_B = 1.0$ and $r_C = 0.8$. The experimental data are given by the open points for the three feed compositions studied.

chlorine,[18] so BEE is resolved from CEE and BEC is resolved from CEC.

The appropriate relationships between observed carbon sequence types and monomer sequence types for this region are

$$P_{\text{obsd}}(00000) = p(\text{EEE}) + \tfrac{1}{2}p(\text{EEV})$$

$$P_{\text{obsd}}(10000 + 00001) = \tfrac{1}{2}p(\text{VEE}) + \tfrac{1}{2}p(\text{EEV})$$

$$P_{\text{obsd}}(10001) = \tfrac{1}{2}p(\text{VEV})$$

Thus the full set of triad monomer sequence probabilities can be derived for the three partially reduced copolymers, excluding the sequences BBB, BBC, BBE, CBC, and BEB that were eliminated by the reduction process. The triad distribution in the parent copolymers follows by simply changing E to B in the probability table, since the reaction was controlled to ensure that a negligible number of C units was converted to E.

Figure 12 shows the observed triad sequence data superimposed on the sequence distribution curves computed from the first-order Markov model with $r_B = 1.0$ and $r_C = 0.8$. This pair of reactivity ratios gave the best fit and agrees closely with the literature values of 1.05 and 0.83.[19] The corresponding values computed by the Q–e scheme are 0.95 and 0.86.[20]

In summary, we find that the VB–VC system is quite similar to the VB_2–VC_2 system, in that both copolymerizations follow nearly ideal Bernoullian statistics. Evidently bromine and chlorine have very similar effects on monomer and radical reactivities in these free-radical copolymerizations. In both cases the chlorinated monomer prefers to add to the brominated chain radical, so the additional steric constraint imposed by the larger bromine substituent appears to have no significant influence on this addition step. Reductive debromination has proven to be a very useful chemical technique to facilitate the NMR analysis of microstructure in VB–VC cpolymers.

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Registry No. PVCF (homopolymer), 67885-24-9; PVBC, 100515-16-0; $(\text{VB}_2)\cdot(\text{VC}_2)$ (copolymer), 91651-52-4; (VB)·(VC) (copolymer), 30875-00-4; PVF_2, 24937-79-9; PVC_2, 9002-85-1; PVB_2, 51736-72-2; VB_2, 593-92-0; VF_2, 75-38-7; VB, 593-60-2; VC, 75-01-4.

References and Notes

(1) Koenig, J. L. "Chemical Microstructure of Polymer Chains"; Wiley-Interscience: New York, 1980.
(2) Randall, J. C. "Polymer Sequence Determination"; Academic Press: New York, 1977.
(3) Bovey, F. A. "Chain Structure and Conformation of Macromolecules"; Academic Press: New York, 1982.
(4) Cais, R. E.; Kometani, J. M. *ACS Symp. Ser.* **1984**, *No. 247*, 153–165.
(5) Cais, R. E.; Brown, W. L. *Macromolecules* **1980**, *13*, 801–806.
(6) Cais, R. E.; Kometani, J. M. *Macromolecules* **1982**, *15*, 954–960.
(7) Blitz, H. *Ber. Dtsch. Chem. Ges.* **1902**, *35*, 3524–3528.
(8) Hjertberg, T.; Wendel, A. *Polymer* **1982**, *23*, 1641–1645.
(9) Schilling, F. C. *J. Magn. Reson.* **1982**, *47*, 61–67.
(10) Wessling, R. A. *J. Appl. Polym. Sci.* **1970**, *14*, 1531–1545.
(11) Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* **1982**, *48*, 323–327.
(12) Kelen, T.; Tüdös, F. *J. Macromol. Sci., Chem.* **1975**, *A9*, 1–27.
(13) Bovey, F. A. "High Resolution NMR of Macromolecules"; Academic Press: New York, 1972.
(14) Wichterle, O.; Zelinka, J. *Chem. Listy* **1957**, *51*, 2146–2148.
(15) Schilling, F. C.; Tonelli, A. E.; Valenciano, M. *Macromolecules* **1985**, *18*, 356–360.
(16) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047–7055.
(17) Cais, R. E.; Sloane, N. J. A. *Polymer* **1983**, *24*, 179–187.
(18) Dostovalova, V. I.; Velichko, F. K.; Vasil'eva, T. T.; Kruglova, N. V.; Freidlina, R. Kh. *Org. Magn. Reson.* **1981**, *16*, 251–260.
(19) Michel, A.; Schmidt, G.; Guyot, A. *J. Macromol. Sci., Chem.* **1973**, *A7*, 1279–1296.
(20) Young, L. J. In "Polymer Handbook" 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1975; pp II-387–II-404.