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THE MICROSTRUCTURE OF COPOLYMERS OF VINYL CHLORIDE WITH ETHYLENE, PROPYLENE, AND ISOBUTYLENE

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ABSTRACT

Copolymers of vinyl chloride with isobutylene, propylene, and ethylene, ranging in composition from 1 to 10 mol% alkene, have been prepared by free-radical polymerization at 50°C. The polymers have been characterized by elemental analysis, gel permeation chromatography (GPC), ^{13}C NMR, and differential scanning calorimetry (DSC). Models for various sequence distributions are used to calculate the chemical shifts in the ^{13}C-NMR spectra by the Lindeman-Adams additivity rule. The spectra of the copolymers with 0.8 to 3.2 mol% ethylene are best fit when a random sequence distribution is used. The copolymer with 7.7 mol% ethylene is found to have 10% of comonomer in block-of-two arrangements. The calculations for the propylene and isobutylene copolymers indicate a random comonomer distribution although other arrangements cannot be ruled out unequivocally. For all copolymers, a single T_g is obtained at all compositions, which is consistent with the ^{13}C-NMR data.

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INTRODUCTION

Although poly(vinyl chloride) (PVC) consists of chemically simple monomer units, subtle differences in its microstructure can affect its properties greatly. The presence of even small quantities of certain anomalous structures, introduced during polymerization, storage, or processing, can dramatically affect its thermal stability [1, 2]. Even differences in stereochemical configuration that result from changes in the polymerization conditions can alter the physical and chemical properties [3, 4].

For more than 50 years a major problem in studies on the thermal stability of PVC has been the diversity of samples used and the incomplete characterization of the polymers. This has given rise to apparently contradictory results. An IUPAC working committee has attempted to resolve such matters by simultaneous studies in various laboratories on given PVC samples [5]. Also, the advent of more sophisticated instruments of high resolution has contributed important knowledge of the microstructure of the PVC and of vinyl chloride copolymers [5-9] and permitted better identification of the structural defects contributing to thermal instability [5, 10, 11].

The incorporation of comonomers into the vinyl chloride sequences can modify the physical and chemical properties. For example, Gupta and St. Pierre showed that copolymerization of vinyl chloride with 2-chloropropylene introduces tertiary chlorines that accelerate thermal decomposition [12]. Similarly, copolymerization with acetylene decreases the thermal stability because of the presence of added double bonds [13]. On the other hand, the vinyl chloride copolymers with ethylene and propylene have been reported to have improved heat stability characteristics over comparable PVC homopolymers [4, 14]. However, there are no studies on the effect of systematic changes in comonomer content on the microstructure, physical properties, and thermal stability.

In this study, copolymers of vinyl chloride with ethylene, propylene, and isobutylene were synthesized and characterized in terms of composition, molecular weight, glass-transition temperature, and sequence distribution, the latter by ^{13}C NMR. It is part of a continuing study of the relationship between the microstructure of homo- and copolymers of vinyl chloride and their physical and chemical properties.

EXPERIMENTAL

A. Synthesis

A vacuum system (ultimate pressure < 0.001 torr) was used to purify and to transfer the monomers. Vinyl chloride (commercial grade, donated by Esso Applications Laboratory, Sarnia, Ontario) was passed through a scrubber containing KOH pellets followed by Drierite, was degassed by repeated melt-thaw cycles, and was then distilled into an evacuated, preweighed stainless-steel reaction vessel (volume 500 cm^3) that had been loaded previously with a known weight of the free-radical initiator 2,2-azobis(2-methylpropionitrile) (Aldrich Chemical Co.). For the synthesis of the copolymers, the degassed comonomer [isobutylene, propylene, or ethylene (Matheson, commercial grade)] was also distilled into the reaction vessel and its weight was determined. The conditions used for the various polymerizations are summarized in Table 1.

B. Purification

The samples were precipitated three times from peroxide-free tetrahydrofuran (THF) solution by the dropwise addition of ice-cold methanol while the solution was being stirred. The final solvent removal was done *in vacuo* at 40°C for 2 h.

C. Characterization

1. Elemental Analysis

The samples were sent to Schwarzkopf Micro Analytical Laboratory Inc., New York, for the analysis of chlorine content. The comonomer contents, calculated on the basis of chlorine content, are given in Table 1.

An ethylene copolymer (0.8%) was arbitrarily chosen for the analysis of nitrogen content as a test for initiator residue. Duplicate tests failed to indicate any nitrogen above the detection limit, which was reported to be 0.2 wt%.

2. Molecular Weights

Both the $\bar{M}_n$ and $\bar{M}_w$ values (Table 1) were determined at room temperature by using a gel permeation chromatograph composed of a Waters pump

TABLE 1. Conditions for Polymerization of Alkene-Vinyl Chloride Copolymers ($T = 50°C$)

AIBN, wt%	VC, g	Comonomer, g	Duration, h	Yield, %	Cl,[a] wt%	Comonomer, mol%	Molecular weight × 10^{-4} $\bar{M}_n$	Molecular weight × 10^{-4} $\bar{M}_w$
				PVC				
0.0138	224	–	16.25	18	56.28[b] 56.65[b]	–	9.1 ± 0.5	16.7 ± 0.5
				Ethylene-Vinyl Chloride				
0.0148	264	16.5	16.0	5.9	56.41[b] 56.25[b]	0.8 ± 0.3	8.6 ± 0.9	13.5 ± 0.4
0.0153	147	13.8	16.0	5.6	55.59[b] 55.80[b]	3.2 ± 0.4	6.4 ± 0.1	12.5 ± 0.1
0.0133	221	29.6	16.0	2.0	54.60 54.33	7.7 ± 0.5	6.7 ± 0.4	10.0 ± 0.3
				Propylene-Vinyl Chloride				
0.0153	249	10.1	16.0	14	56.42[b] 56.22[b]	0.5 ± 0.3	6.8 ± 0.4	11.7 ± 0.3
0.0143	214	3.5	16.0	12	56.03	1.3	7.5 ± 0.2	15.4 ± 0.1
0.0144	145	20.6	12.25	6.1	54.86	4.3	5.7 ± 0.7	9.3 ± 0.2
0.0128	241	42.3	16.0	2.5	53.58[b] 53.36[b]	7.2 ± 0.3	7.4 ± 0.3	12.4 ± 0.1

			Isobutylene-Vinyl Chloride					
0.0173	161	2.4	16.5	9.8	55.97	1.1	7.0 ± 0.3	10.4 ± 0.4
0.0148	261	10.3	18.25	2.7	55.42	2.2	3.9 ± 0.1	7.3 ± 0.1
0.0153	236[c]	8.9	18.0	3.7	54.44	4.1	3.1 ± 0.1	5.6 ± 0.1
0.0130	221[c]	20.9	18.0	1.6	52.03	8.7	1.8 ± 0.1	2.5 ± 0.1
0.0141	234[c]	–	18.0	2.1	51.23[b] 50.93[b]	10.3 ± 0.3	1.4 ± 0.1	2.3 ± 0.1

[a] Elemental analysis.

[b] Duplicates

[c] Weight of vinyl chloride is less than that reported, while the weight of isobutylene is correspondingly more, due to the reuse of excess gas from previous polymerizations.

(Model 6000A), a Waters U6K injector, a bank of five Waters Microstyragel columns with quoted permeabilities in the order 10^6, 10^5, 10^4, 10^3, and 500 Å, a Perkin-Elmer refractometer and a Chromatix KMX6 low-angle laser light-scattering spectrometer (LALLS), successively. Polystyrene standards were used for the calibrations. A Brice Phoenix differential refractometer was used to determine the refractive index increments (*dn/dc*) of dilute solutions of polymer in THF. Data treatment was done with a Digital RT11 computer with a routine program (Chromatrix LDS Software).

3. Glass-Transition Temperatures

The T_g's were determined with a Perkin-Elmer differential scanning calorimeter (Model DSC-2C) equipped with a thermal analysis data station. To produce a uniform thermal history, the samples (5-10 mg) were first heated, at a rate of 20 K/min, to 85 or 90°C, maintained isothermally for approximately 20 min, then cooled at a rate of 320 K/min to a subambient temperature ~20 K lower than the T_g of the pure homopolymer of the comonomers [15]. The T_g was obtained from a second heating, at a scanning rate of 20 K/min, to 100°C. An uncertainty in the T_g of ±0.8 K was estimated from duplicate determinations.

4. ^{13}C NMR

The pulsed Fourier-transform ^{13}C-NMR spectra were obtained with a Varian XL 300 spectrometer, operating at 75.4290 MHz with a spectral width of 16 500 Hz. The acquisition time was 0.9 s and a pulse angle of 60° was normally used. Proton noise decoupling was utilized. To obtain spectra suitable for quantitative analysis, the delay times between sample pulses were varied between 1.0 and 5.0 s, which ensured complete carbon atom relaxation. The spectra were taken at 110°C. To obtain a satisfactory signal-to-noise ratio, 3000 to 5000 scans were required.

The solutions, contained in 10 mm sample tubes, were 15-20% (w/v) in 4:1 1,2,4-trichlorobenzene:*p*-dioxane-d_8 for a "lock" signal. Alternatively, the solutions were prepared in 1,2,4-trichlorobenzene with dimethylsulfoxide (DMSO-d_6) in a concentric tube for a "lock" signal. Hexamethyldisiloxane (HMDS) was used as an internal reference (2.0 ppm vs TMS).

RESULTS AND DISCUSSION

A. Sequence Analysis by ^{13}C NMR

^{13}C NMR is the method of choice for characterization of polymer microstructure [6-9, 16, 17]. Studies of paraffinic hydrocarbons and their derivatives have demonstrated that the chemical shifts induced on a carbon by neighboring functional groups are nearly additive [18]. For example, it is well known that each carbon substituent α or β to the observed carbon produces a downfield shift of 9 ppm (deshielding effect), while γ-carbon substituents result in an upfield shift of ~2 to 3 ppm [17].

By using the Lindeman-Adams rule [19], the chemical shift, $\delta_c(k)$, of an observed carbon k can be calculated according to

$$\delta_c(k) = A_n + \sum_{m=0}^{2} N_m{}^{a}\alpha_{nm} + N^{\gamma}\gamma_n + N^{\delta}\delta_n, \qquad (1)$$

where A_n, α_{nm}, γ_n, and δ_n are empirical parameters derived from a study of a series of 59 alkanes [19], N_m ($m = 0, 1, 2$) is the number of CH_m groups in the α position, n is the number of hydrogens attached to carbon k, N^{δ} is the number of δ-carbons, and N^{γ} is the number of γ-carbons. For substituents other than carbon atoms, the chemical shift can be obtained by calculating the shift of the parent alkane and adding the appropriate substitute parameters [17].

When the empirical constants given by Lindeman and Adams [19] are used to calculate the chemical shift for the methylene carbons of polyethylene, a value of 29.96 ppm is obtained, in excellent agreement with the measured value [7]. However, attempts to fit the spectra of chlorine-containing polymers met with only limited success, in part because values are unavailable to account for certain effects that result from the presence of the Cl atoms. To this end, the following procedures have been adopted.

The expected chemical shift for a methylene carbon in a polymer with chlorines at alternating carbons can be obtained by combining the values obtained for polyethylene and adding corrections that account for the chlorines in the β-positions, i.e., those attached to the α-carbon, and the effect of any chlorines at the γ-position. Previous studies [6] have shown that a single chlorine substituent in the β-position produces a downfield shift of 10.5 ppm. These values are not additive, so that when a second Cl is located on the α-carbon at the other side of the CH_2 group, the total deshielding effect is +19.5 ppm rather than the expected 21.0 ppm. From these values the contribution due to the CHCl group at the γ-position can be derived from the measured chemical shift of the CH_2 in the spectrum of PVC homopolymer, which is centered at 47.5 ppm. The resulting value for the effect on the chemical shift of the methylene carbon due to a CHCl at the γ-position, $\gamma(CH_2,CHCl)$, is -1.0 ppm.

For the methine carbons, fit to the PVC spectrum is obtained by use of the Lindeman-Adams empirical constants and $\gamma(CH,Cl) = -3.0$, as reported previously [6].

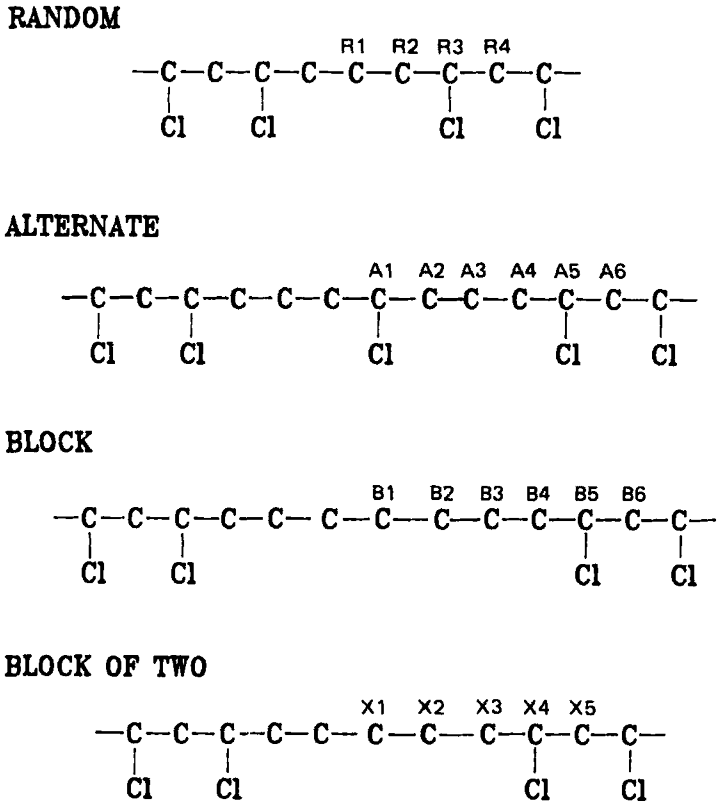


FIG. 1. Models for the microstructure of ethylene-vinyl chloride copolymers considered in the calculation of chemical shifts.

1. Ethylene-Vinyl Chloride Copolymers

Models corresponding to "random," "alternating," "block," and "block-of-two" variations of comonomer sequences, illustrated in Fig. 1, were considered as possible microstructures for the ethylene-vinyl chloride (E-VC) copolymers. The expected chemical shifts were calculated for various possible comonomer sequence distributions by using the Lindeman-Adams additivity rules together with the γ-substituent parameters described above. The ^{13}C-NMR spectra of the homopolymer and of two E-VC copolymers are shown in Fig. 2. Two principal regions are evident: 1) The methine carbon resonances between 53 and 64 ppm, and 2) the methylene carbon resonances between 23 and 48 ppm.

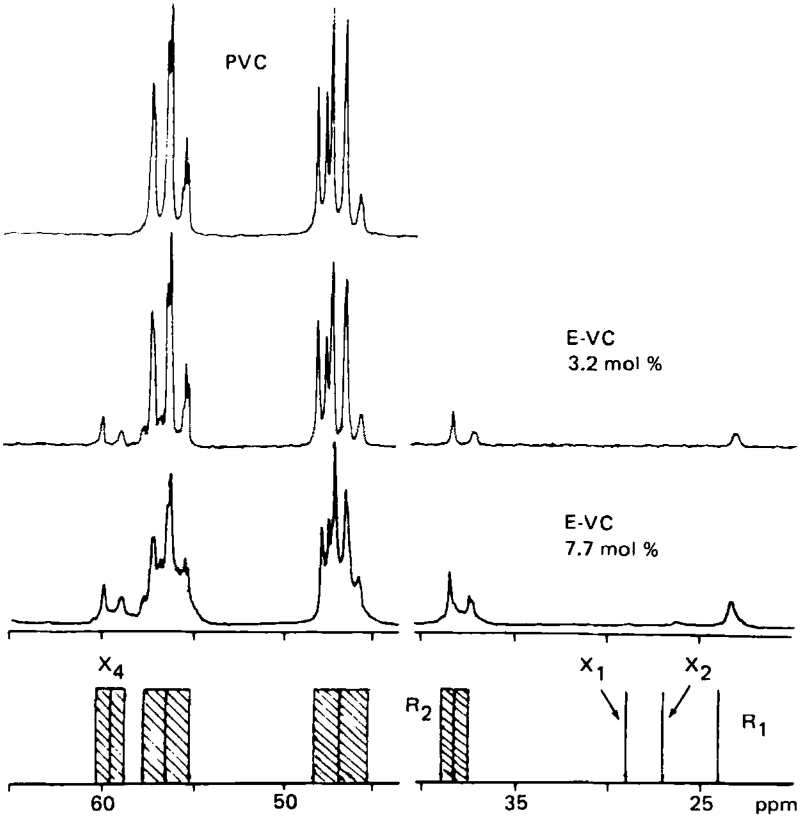


FIG. 2. The ^{13}C-NMR spectra of PVC and ethylene-vinyl chloride copolymers. The position of the calculated chemical shifts for the random arrangement is shown at the bottom.

To begin the analysis of sequence distribution, attention is focused on the methine region. For an "alternate" arrangement, –E–VC–E– bonded to long VC sequences, the calculations predict a chemical shift at 63.5 ppm for the methine resonance of the isolated VC units corresponding to the A1 methine group (Fig. 1). (The calculation includes a contribution of 31.0 ppm due to the Cl in the α position [6].) Since the spectra of the E-VC copolymers give no evidence of a corresponding chemical shift, the occurrence of "alternate" sequence arrangements can be ruled out.

A calculated shift ~3 ppm downfield from that for the methine carbon resonance of the long VC sequences is obtained when one, a block, or a block-of-two ethylene units are vicinal to the VC units. This chemical shift, centered at 59.7 ppm, corresponds to the methine groups R3, B5, or X4 in the "random," "block," or "block-of-two" models. It can be assigned to the peaks, separated by 1 ppm due to the VC stereosequences, at 59.1 and 60.1 ppm in the E-VC spectra. Obviously, the chemical shifts for these methine carbons do not permit a choice between these models.

For the remaining models, the values predicted for the chemical shifts of the methylene carbon resonances lie in five regions, centered at 24.0, 27.0, 30.0, 38.8, and 47.5 ppm. The last corresponds to the methylene resonances of the long VC sequences, found in the region of 47-49 ppm in the spectrum of PVC homopolymer.

For the central methylene group, represented as carbon R1 in the "random" model, the chemical shift is expected to be 24.0 ppm, corresponding to the peak at 23.4 ppm in the ^{13}C-NMR spectra (Fig. 2). For the methylene group vicinal to the methine carbon of the long sequences of VC units, represented as carbon R2 in the "random" model, the calculated chemical shift is 38.8 ppm, in good agreement with the two peaks centered at 38.1 ppm. The presence of two resonance peaks is expected because of the sensitivity of these methylene groups to the stereochemical arrangements of the VC units. The calculated chemical shift for the methylene carbons R4, A6, B6, or X5 in the various models is 47.2 ppm, overlapping with the methylene carbon resonances of the long VC sequences. Because of this overlap, distinct assignments are not possible.

For the central methylene groups in the "block" (B1 or B2) or in the "block-of-two" models (X1), the calculated chemical shift is 30.0. No corresponding peak appears in the NMR spectra of the copolymers with 0.8 and 3.2 mol% ethylene. This confirms that these copolymers do not contain blocks of ethylene or, if there are any, that they must be present in very low concentration. In fact, the spectrum for the copolymer with 7.7 mol% ethylene has two small peaks, centered at 26.6 and 29.0 ppm, that indicate the presence of some ethylene blocks. The peak appearing at 29.0 ppm probably corresponds to the calculated chemical shifts for the methylene carbons B1 and B2 at 30.0 ppm, or carbon X1 at 29.3 ppm, while the peak at 26.6 ppm fits the calculated values for carbons B3 or X2 at 27.0 ppm in the "block" or "block-of-two" models, respectively. For the "block" model there are three equivalent carbons, one labeled B1 and two B2, with resonance at ~29 ppm and two carbons B3 with resonance at 26.6 ppm, so that the expected ratio for the areas of the peaks at 26.6 and 29-30 ppm is 3:2. However, the "block-of-two" arrangement has one X1 carbon and two X2 carbons. Hence, the areas of peaks with resonance at 26.6 and 29-30 ppm are expected to be in the ratio 1:2, as is observed. Consequently, the blocks must consist exclusively of two ethylene units.

The calculated chemical shifts for the various carbons, as labeled in the "random" model, are plotted on the "stick" diagram beneath the spectra in Fig. 2. Based on the calculated chemical shifts of the various carbons of the E-VC copolymer models, it can be concluded that the "random" model best fits the spectra.

Tonelli et al. successfully predicted ^{13}C-NMR chemical shifts for the various carbon atoms in polypropylene and its oligomers [20-22], ethylene-propylene copolymers [23], ethylene-vinyl chloride copolymers [7], polystyrene and its oligomers [24], several fluorocarbon polymers [25], and, recently, propylene-vinyl chloride copolymers by calculations based on γ-gauche effect [8]. This method considers that only those γ-substituents that have a gauche arrangement contribute to the shielding effect of the observed carbon. By the rotational isomeric state (RIS) theory [25-27], it was possible to calculate the bond rotational probabilities and evaluate the number of γ-gauche interactions for a given carbon atom. Comparison of the chemical shifts calculated by Tonelli et al. [7] with the spectra obtained in this study supports the conclusion that the E-VC copolymers have mostly random sequence arrangements at all comonomer concentrations.

Quantitative Analysis. Since the regions of resonance for the methine and methylene carbons are well defined, the comonomer composition of the E-VC copolymers is readily obtained from the integrated peaks areas [6]. For PVC homopolymer, the integral sum, I(CH), of the methine carbon resonances in the 55-57 ppm region must equal the integral sum, $I(CH_2)$, of the methylene carbon resonances in the 47-49 ppm region. For the E-VC copolymers, the methine carbon resonances are in the 55-60 ppm region and the CH_2 carbon resonances are in the 20-50 ppm region. Hence, the mole percent of the ethylene units, X_E, in the E-VC copolymer can be obtained from

$$X_E = \frac{100[I(CH_2) - I(CH)]}{I(CH_2) + I(CH)}. \tag{2}$$

The ethylene contents obtained by this method are 0.9, 3.3, and 7.7 (± 0.2) mol%, in excellent agreement with the values of 0.8, 3.2, and 7.7 mol%, respectively, obtained by elemental analysis.

The mole fraction "block-of-two" ethylene units, X_{B2}, in the 7.7 mol% E-VC copolymer can be determined by comparing the methylene integral value for the Rl carbon in the "random" model with the integral values for the methylene X1 and X2 carbons in the "block-of-two" model. Thus,

$$X_{B2} = X_E \frac{I(X1) + I(X2)/2}{I(R1) + I(X1) + I(X2)/2}. \tag{3}$$

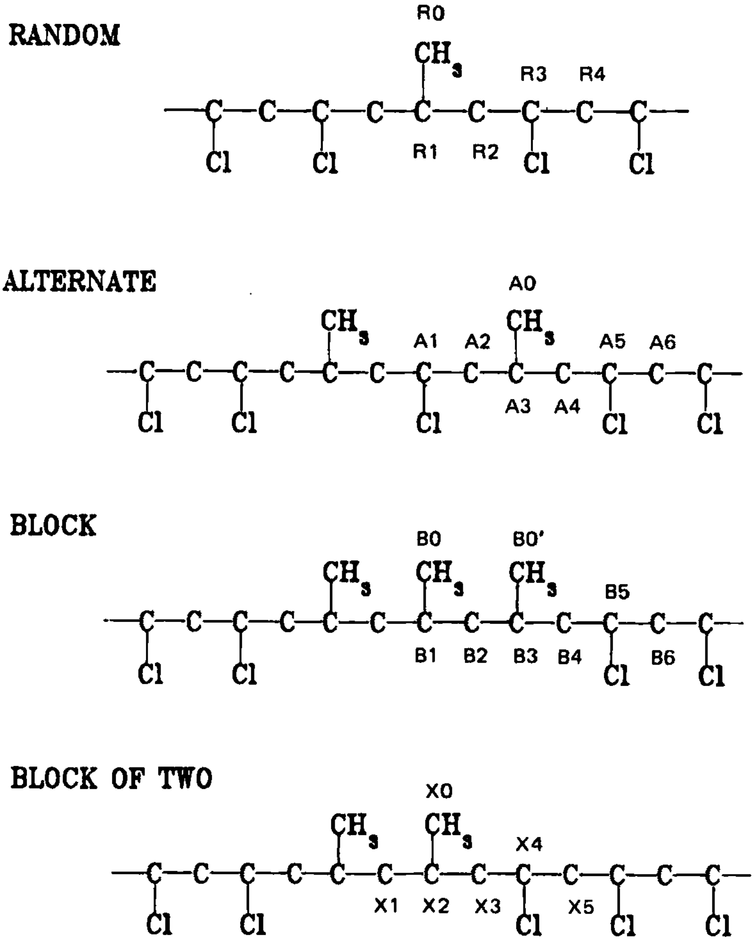


FIG. 3. Models for the microstructure of propylene-vinyl chloride copolymers considered in the calculation of chemical shifts.

By using Expressions (2) and (3), it was found that the comonomer distribution for the E-VC 7.7 mol% is 90% random and 10% "block-of-two" arrangements.

2. Propylene-Vinyl Chloride Copolymers

The additivity rules have also been used to predict chemical shifts for the propylene-vinyl chloride (P-VC) copolymers. Only head-to-tail arrangements of propylene and vinyl chloride units were considered as possible models, illustrated in Fig. 3, for the microstructure. The calculated chemical shifts for the various carbons represented in the "random" model are plotted in Fig. 4, be-

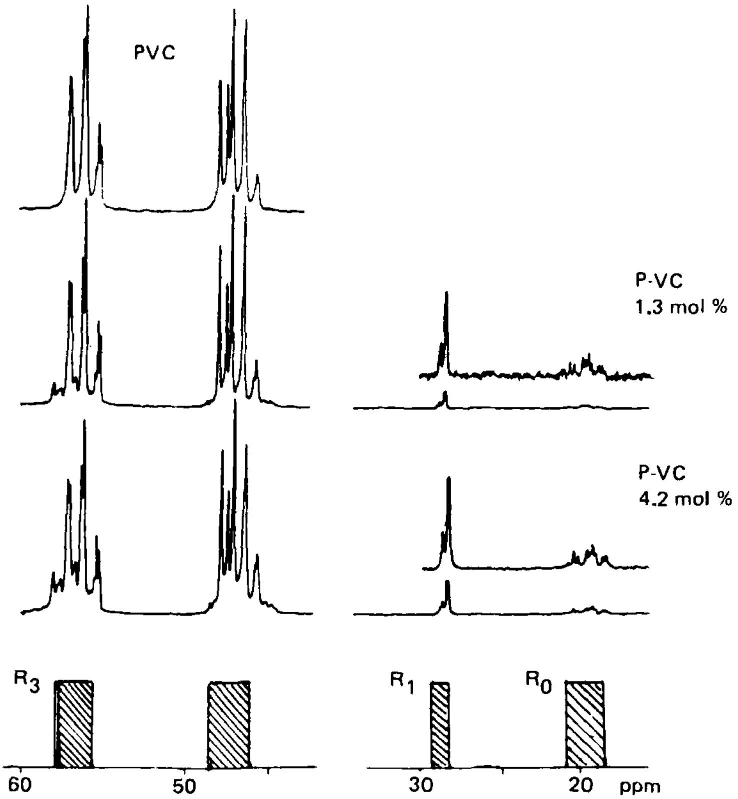
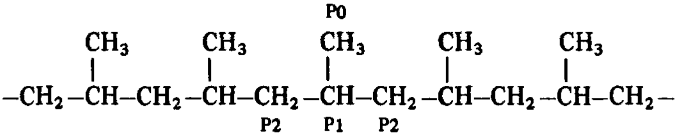


FIG. 4. The ^{13}C-NMR spectra of PVC and propylene-vinyl chloride copolymers. The position of the calculated chemical shifts for the random arrangement is shown at the bottom.

neath the ^{13}C-NMR spectra of P-VC copolymers of various propylene content. The γ-substituent values derived previously for the E-VC copolymers were also used for the P-VC copolymers. Thus, $\gamma(CH,Cl) = -3.0$, $\gamma(CH_2,CHCl) = \gamma(CH_2,CHCH_3) = -1.0$, and the Lindeman-Adams $\gamma(CH,CH_2) = \gamma(CH,CH_3) = 2.0$ and $\gamma(CH_3,CH) = -3.0$ values have been used.

To assist in the assignment of the chemical shifts of the P-VC copolymers, the chemical shifts for the polypropylene homopolymer were calculated by using the model



$$-CH_2-\overset{\overset{CH_3}{|}}{CH}-\underset{P2}{CH_2}-\overset{\overset{\overset{P0}{CH_3}}{|}}{\underset{P1}{CH}}-\underset{P2}{CH_2}-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-$$

For the homopolymer, the calculated chemical shift for the methylene carbon, carbon P2, is 47.7 ppm. For the P-VC copolymers, the calculated chemical shift for the methylene carbon vicinal to the methylated methine carbons, represented by carbons R2, A2, A4, B2, B4, X1, and X3 in the various models (Fig. 3), range from 47.2 to 47.5 ppm. Multiple resonance peaks are expected because of the sensitivity of the methylene carbon to stereochemical arrangements of the vicinal VC units. A large number of resonances of minor intensity, downfield and upfield and overlapping with the methylene resonances of the VC units, are evident in the 45-49 ppm region of the ^{13}C-NMR spectra (Fig. 4) and consequently give no information concerning sequence arrangement.

For the methyl carbon P0 of the homopolymer, the calculated chemical shift is 20.6. Zambelli and Bovey have assigned the corresponding stereochemical shifts observed at 21.55, 20.85, and 20.17 ppm of polypropylene to the methyl mm, mr, and rr triad sequences [28]. For the methyl carbon resonances, represented by R0, A0, B0 or B0′, and X0, the calculated chemical shifts range from 19.6 to 20.6 ppm for the different models considered. The spectra of the P-VC copolymers contain multiple chemical shifts ranging from 19.1 to 20.7 ppm that are undoubtedly due to these methyl resonances. Nevertheless, the close proximity of the chemical shifts calculated for the various models precludes a choice of sequence arrangements.

For propylene homopolymer, the calculated chemical shift for the methine carbon, represented by carbon P1, is 28.4 ppm, which compares favorably with the reported peaks at 28.92 and 28.47 ppm [16]. The chemical shifts of the methine carbons of the P-VC copolymers are expected to be in two well-defined regions.

Region 1. In the case of the methine carbons with an α-methyl group, represented by carbons R1, A3, B1, or X2 in Fig. 3, the calculated chemical shifts range from 25.7 to 26.2 ppm, corresponding to the two peaks (due to the methine stereosensitivity), with resonance centered at 28.4 ppm and 0.6 ppm width, independent of the propylene content (Fig. 4). This assignment is consistent with the conclusion of Tonelli and Schilling [8] in a recent study by ^{13}C NMR of a vinyl chloride copolymer with 5.1 mol% propylene content. The chemical shift appearing at ~28 ppm was assigned to the methine carbon resonance of the propylene units, as shown by calculations based on the γ-effect method, described previously, assuming random sequence placement.

The difference between the observed chemical shifts of the methylated methine carbons and that obtained by the additivity rule probably reflects steric interactions between the γ-chlorine and the α-methyl substituents of the methine groups. In fact, in branched systems, deviation from simple additivity has been noted previously, and empirical correction factors have been reported for carbon substituents [17, 19]. The introduction of a propylene comonomer into the VC chains probably disturbs the geometry of the VC units vicinal to the propylene and hence gives rise to new steric interactions between the substituent groups [30]. Since this kind of interaction is not considered when the additivity rules are used, it is not surprising that the use of $\gamma(\mathrm{CH,Cl}) = -3.0$ to calculate the chemical shifts for the P-VC copolymers fails to fit the spectra. Indeed, a good fit to the spectra is obtained when $\gamma(\mathrm{CH,Cl}) = -2.0$ is used, which is almost identical to the Lindeman-Adams value of -2.07 ppm for the γ-effect when the substituent is a carbon substituent [19].

The chemical shifts for the methine carbons with a methyl group calculated for the various models are too close together to permit any conclusions about the sequence arrangement.

Region 2. For the methine carbon of the VC units vicinal to propylene units, i.e., carbons R3, A1, B5, or X4, with a Cl atom at the γ-position, the calculated shift is ~2 ppm downfield relative to that calculated for the carbon methine in long VC sequences. The ^{13}C-NMR spectra, Fig. 4, have a corresponding chemical shift at 58.4 ppm, about 2 ppm downfield from the carbon methine resonance of the VC units. However, again the calculated chemical shifts do not permit discrimination between the possible sequence arrangements.

The calculations based on the additivity rules are not sufficiently precise to give detailed information about the sequence distribution of the P-VC copolymers. Since propylene does not homopolymerize under the conditions used to synthesize the copolymers of this study [29], random sequence distribution seems likely, especially at low comonomer content.

Quantitative Analysis. Although the intense, well-defined peak at 28 ppm gives insufficient evidence for an unambiguous determination of the sequence distribution of the P-VC copolymers, it can be used for quantitative determination of the propylene content by comparison of its intensity with that for the methine carbon resonance of the VC units. In fact, it is well established that methine carbons of propylene units show resonance ~31 ppm upfield from the methine resonances of the VC units [6]. In this manner, the integral sum of the methine carbon resonances of the propylene units, $I(CH-CH_3)$, and of the VC units, $I(CH-Cl)$, permits a determination of the mole percent of propylene, X_P, from

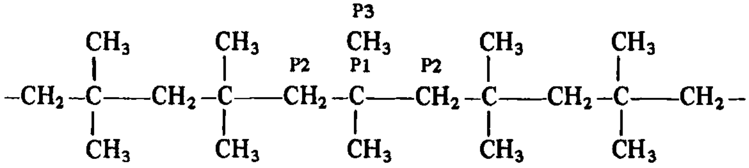
$$X_P = \frac{100[I(CH-CH_3)]}{[I(CH-CH_3) + I(CH-Cl)]}. \qquad (4)$$

The values obtained are 0.4, 3.9, and 7.2 (± 0.2) mol% propylene compared to 0.5, 4.2, and 7.2 mol%, respectively, obtained by elemental analysis.

3. Isobutylene-Vinyl Chloride Copolymers

Only head-to-tail arrangements of isobutylene and vinyl chloride units have been considered. The "random," "alternate," "block," and "block-of-two" variations of comonomer sequence, shown in Fig. 5, were considered as possible models of the microstructure of the isobutylene-vinyl chloride (iB-VC) copolymers.

To assist in the assignment of the chemical shifts of the iB-VC copolymers, a sample of polyisobutylene (Polysciences, #9897, MW 2700) was characterized by ^{13}C NMR. The spectrum is shown in Fig. 6. The chemical shifts, calculated by the additivity rule, for the various carbons of the isobutylene homopolymer model shown below are in three different well-defined regions, corresponding to the carbon resonance of quaternary carbon P1 at 36.4 ppm, the methylene carbon P2 at 54.3 ppm, and the methyl carbon P3 at 29.2 ppm.



$$-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-\overset{P2}{CH_2}-\underset{CH_3}{\overset{\overset{P3}{CH_3}}{\overset{P1}{C}}}-\overset{P2}{CH_2}-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-$$

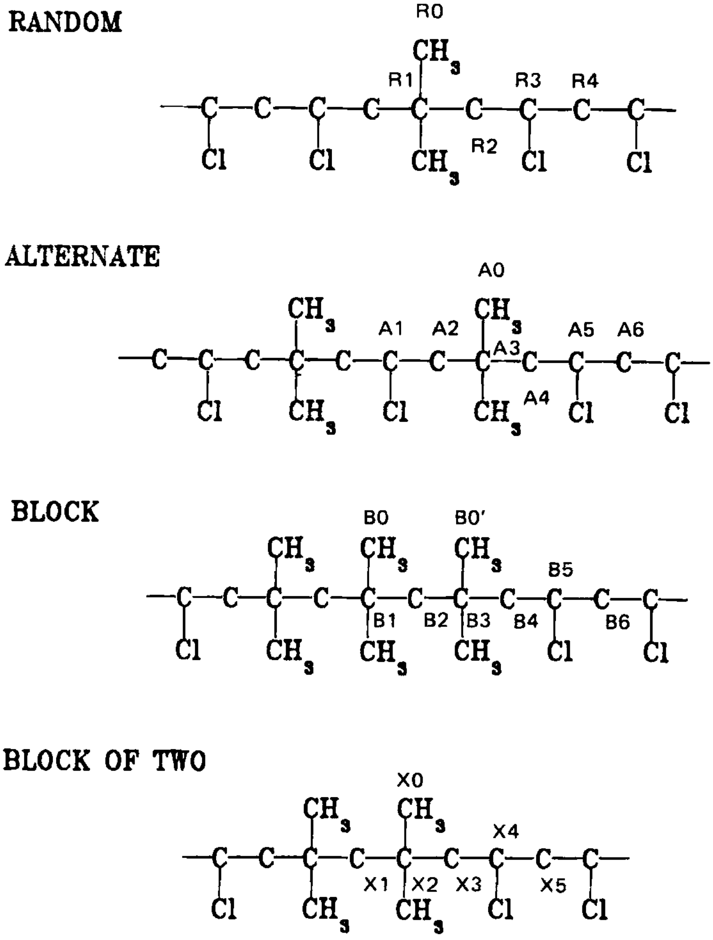


FIG. 5. Models for the microstructure of isobutylene-vinyl chloride copolymers considered in the calculation of chemical shifts.

Only qualitative agreement with the spectrum is obtained. The peak at 38.2 ppm can be assigned to the quaternary carbon resonance (P1) and that at 31.3 ppm to the carbon resonance of methyl groups (P3). In both cases there is a downfield shift of ~2 ppm from the calculated chemical shifts. The peak centered at 59.6 ppm can be assigned to the methylene units (P2), so that the difference is 5.3 ppm downfield from the calculated chemical shift. Such

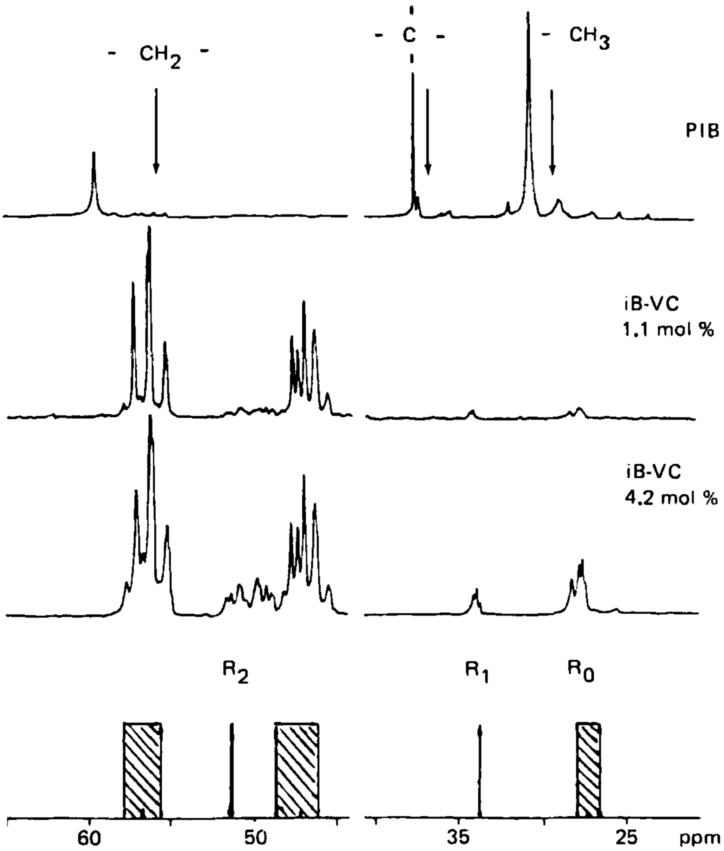


FIG. 6. The ^{13}C-NMR spectra of polyisobutylene (PIB) and isobutylene-vinyl chloride copolymers. The arrows in the PIB spectrum indicate the positions predicted by additivity rules for the CH_2, quaternary carbon, and CH_3 resonances. The positions of the calculated chemical shifts for the random arrangement are shown at the bottom.

"anomalous chemical shifts" have been attributed to the presence of "crowded" methyl groups [31, 32]. In fact, it has been shown that the presence of *gem*-dimethyl groups in long segments crowded by methyls, as occurs with the polyisobutylene chain, gives rise to long-range effects that cannot be considered as truly additive contributions [31]. In spite of these anomalous effects, the additivity rule is useful for the preliminary assignment of chemical shifts.

The Lindeman-Adams study [19] showed that the chemical shifts of an isolated quaternary carbon atom in an alkane chain lie within a relatively narrow range which indicates that the neighboring carbon atoms have little effect on its chemical shift. They found that instead of an upfield "shielding effect" for γ-substituents, all carbon constituents exhibit a small downfield effect of $\gamma(C,C) = 0.68$ ppm.

The differences between the calculated and the experimental values for chemical shifts of the methylene carbons (P2) of polyisobutylene can be interpreted as long-range effects due to the *gem*-dimethyl groups, as assumed by Corno et al. [31]. Use of the Lindeman-Adams value of $\gamma(CH_2,C) = -2.69$ to calculate the effect on the chemical shift of methylene carbon due to any carbon substituent at the γ-position requires a strong δ-effect of +1.57, i.e., much higher than the Lindeman-Adams value of $\delta(CH_2) = 0.25$.

The calculated chemical shifts for the iB-VC copolymers, found from the substituent values derived above, are compared with the ^{13}C-NMR spectra in Fig. 6. For the random or alternate arrangement the chemical shift predicted for the quaternary carbon of isobutylene is ~33.7 ppm. It is expected to be shifted somewhat downfield, in the 35-36.4 ppm region, for a "block" or "block-of-two" arrangement. The spectra show a triplet centered at 34.04 ppm that can be assigned to this quaternary carbon. The occurrence of a triplet is indicative of stereochemical sensitivity. The agreement between the predicted and the experimental chemical shift is a strong argument to consider the "random" or "alternate" models as the more likely sequence arrangements. This is supported by a comparison of the spectrum of the copolymer of low isobutylene content (4.2 mol%), for which a random sequence distribution is expected to predominate, with that of 10.2 mol% isobutylene content which shows that the peak corresponding to the quaternary carbon resonance appears at exactly the same position and that there is no additional peak downfield, as would be expected for a "block" or a "block-of-two" sequence.

For all the models considered, the calculated chemical shift of the methine carbon is expected to overlap with the methine carbon resonance of the long VC sequences. Consequently, these resonances offer no information about the sequence distribution.

The methylene chemical shifts are expected to be extremely sensitive to the kind of vicinal carbon. For isolated isobutylene units, as in the random arrangement, the methylene groups on either side of the quaternary carbon (R2) are equivalent, and the chemical shift is expected to be at 48.6 ppm. The ^{13}C-NMR spectra are complex in this region (Fig. 6), with a series of peaks centered at 50.3 ppm with a width of 2.8 ppm. These peaks can be assigned to the methylene carbon resonance, and the complex pattern can be explained in terms of the stereochemical sensitivity of the methylene groups, which is also observed for the methylene groups (carbon R4) of the VC units. In the case of an "alternate" arrangement, the methylene carbon A2, in Fig. 5, is expected to have a chemical shift ~0.5 ppm downfield, but it could overlap with the A4 or R2 methylene carbon resonances. For the "block" or the "block-of-two" arrangement, the internal methyl group, carbon B2 or X1, should have a chemical shift ~4 ppm downfield at 53.8 ppm. The spectra show no evidence of overlap with the methine carbon resonances, so that "block" or "block-of-two" sequence arrangements can be ruled out.

The chemical shifts for the methyl groups are expected to be in the 27-29 ppm region for the different models. For a "random" or an "alternate" arrangement, the predicted chemical shift is 27.3 ppm. For block copolymers the chemical shift for the internal methyl group, carbon B0, is expected to be 29.2 and 28.3 for the external methyl, carbon B0′. The predicted chemical shift for the methyl carbon X0 of a "block-of-two" arrangement is 28.3 ppm. The spectra have a triplet centered at 27.3 ppm and a singlet at 27.9 ppm. The resonances in this region can be assigned to the methyl carbon of the isobutylene units with the multiplets resulting from the stereochemical sensitivity.

In summary, although it is not possible with the available information to distinguish between random and alternate sequence arrangements, the random arrangement is favored because no difference is seen between the spectra of low and high comonomer content.

To verify the chemical shift assignments, a two-dimensional (2D) NMR experiment was performed. By the use of the double Fourier-transform method it is possible to make a simultaneous measurement of proton and carbon-13 chemical shifts [9], allowing a direct correlation of chemical shifts. The full two-dimensional chemical shift correlation spectrum for the copolymer containing 10.6 mol% isobutylene, Fig. 7, shows that the peaks in the 53-59 ppm region of the ^{13}C-NMR spectrum, assigned to the methine carbon resonances, clearly correlate uniquely with the triplet centered at 4.5 ppm in the proton spectrum. Similarly, the carbon-13 resonances from 44 to 52 ppm, assigned to methylene carbons, and those from 27 to 30 ppm, assigned to the methyl carbons, correlate with proton resonances at 1.7 and 1.0 ppm, respectively. As expected, the carbon-13 resonances at 34 ppm, attributed to the quaternary carbon, have no signal in the proton spectrum. In all cases the heteronuclear two-dimensional experiment confirms the assignment of the chemical shifts given above.

Quantitative Analysis. The mole percent isobutylene of these copolymers, X_{IB}, can be obtained from the integral areas of methine and methylene peaks according to

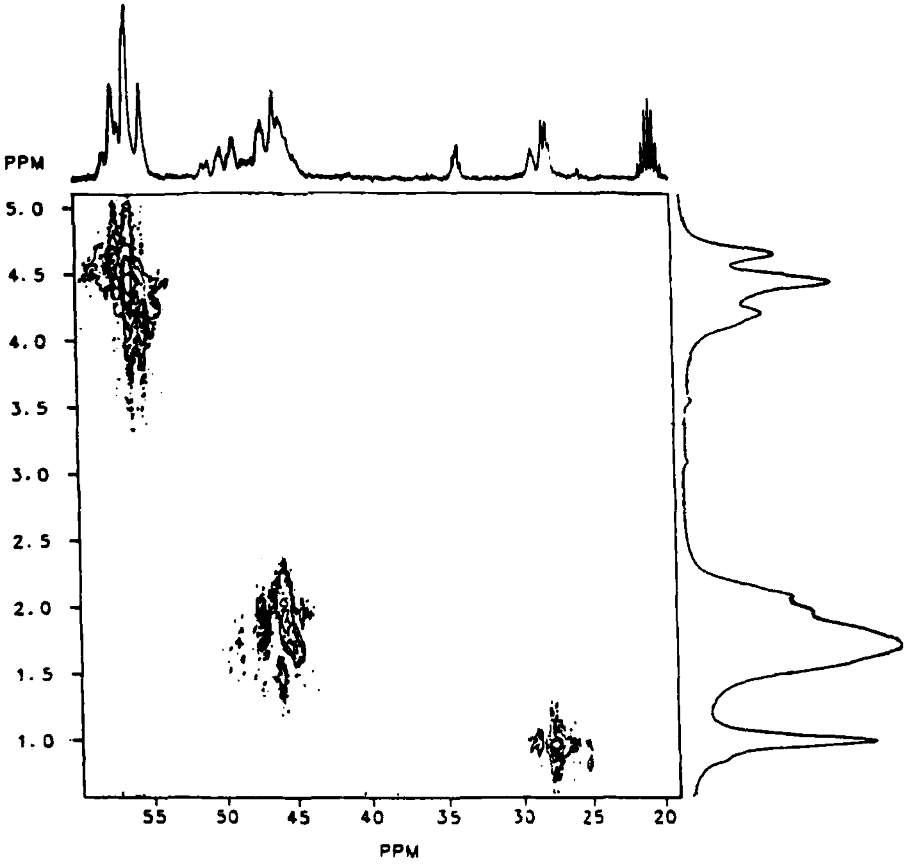


FIG. 7. Heteronuclear ^1H-^{13}C correlation spectrum of the isobutylene-vinyl chloride copolymer containing 10.6 mol% comonomer.

$$X_{iB} = \frac{100[I(CH_2) - I(CH)]}{I(CH_2)} . \tag{5}$$

The compositions by this method are 1.1, 4.3, 8.4, and 10.4 (+ 0.2) mol%, compared to 1.1, 4.1, 8.7, and 10.6 mol%, respectively, obtained by elemental analysis.

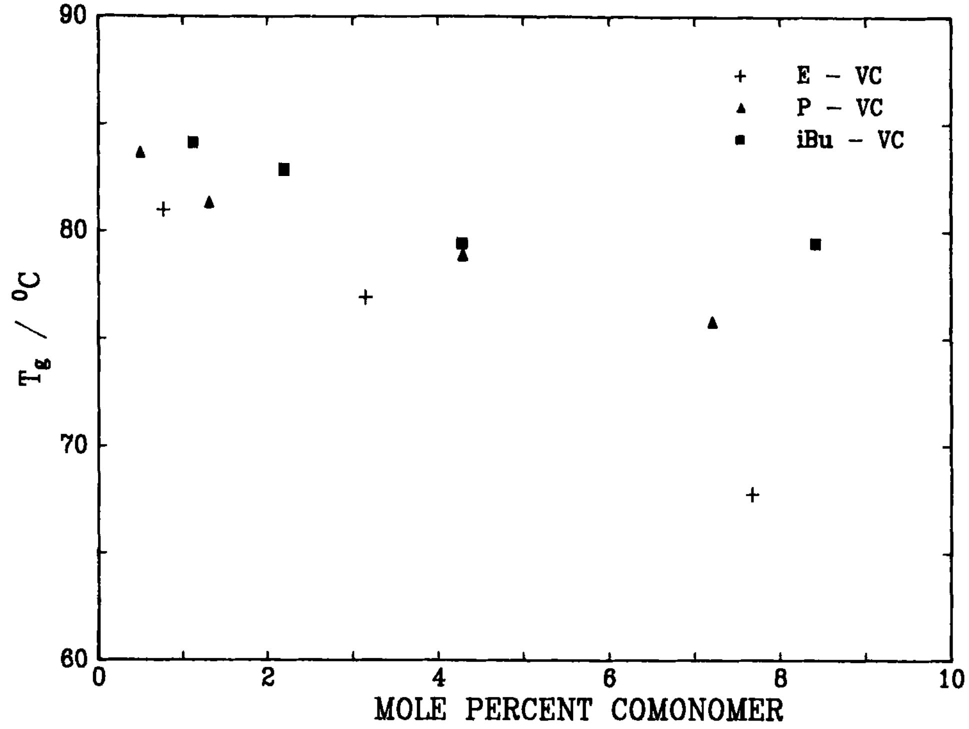


FIG. 8. The effect of an increase in comonomer concentration on the glass-transition temperatures.

B. Thermal Transitions

A single T_g, that decreases regularly with comonomer content, was obtained for all samples (Fig. 8), and no other transitions were observed. This is consistent with the absence of long blocks of comonomer which could crystallize or form some separate amorphous phase, resulting in two T_g's.

The results for the ethylene copolymers are in general agreement with recent studies of Bowmer and Tonelli [33] and Braun et al. [34] for copolymers obtained by reduction with tributyltin hydride. The latter copolymers were shown by ^{13}C-NMR studies to be nearly random.

SUMMARY

Both ^{13}C-NMR and T_g measurements for these alkene copolymers of vinyl chloride discount the possibility of long blocks of comonomer. However, for the E-VC copolymer containing 8 mol% comonomer, short blocks of two are found among long sequences of vinyl chloride.

The applicability of the Lindeman-Adams additivity rule in the assignment of chemical shifts for polymers and copolymers has been demonstrated. In copolymers the monomer placements and distributions can be predicted. Although this method does not consider the effect of stereochemical arrangements, such information can be obtained by two-dimensional (2D) NMR analysis. In fact, hetero- (^{1}H-^{13}C) and homonuclear (^{1}H-^{1}H) experiments have been used successfully in the study of small molecules, of biopolymers and, recently, of polymers. In the present work the heteronuclear 2D experiment provided vital information for the assignment of certain peaks in the iB-VC spectra. Modern high-field NMR instruments are sufficiently sensitive to permit the quantitative determination of even very small amounts of comonomer.

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