chain diffusional processes are of the order of 100–200 kcal.[10] In view of this fact and the fact that, at higher temperatures, W.L.F.-type temperature dependence is obtained for the shift factors corresponding to the primary mechanism, it seems reasonable to assign the primary mechanism to the usual diffusional process associated with the glass transition of nonionic polymers; it seems likely, however, that the mechanism is modified in some way by the ions, since unusually high W.L.F. parameters are obtained.

The secondary relaxation process is likely ionic in its origin. There is theoretical[11] and experimental[6,7] evidence for ion clustering in these ion-containing systems. The activation energies for the secondary mechanism, of the order of 25 kcal, could correspond to the energy required to remove an ion pair from an ionic cluster. Whatever its form, if the secondary mechanism were due to the yielding of ionic structure, it would be expected to correspond to a pure viscosity in the same fashion as bond interchange.[3] In this case, the approximate relationship

$$D(t) \simeq t/\eta \qquad (3)$$

should hold. It can be seen in Figures 4 and 5, by comparison with the hypothetical doubly logarithmic slope of unity, that this is approximately true for each case.

The assignment of viscoelastic mechanisms in these ion-containing polymers requires a more complete investigation. Further discussion of the viscoelastic behavior in these systems will be reserved for future publications.

Conclusions

A general method for the analysis of viscoelastic data from ion-containing polymers in which the breakdown of time–temperature superposition occurs has been presented. Examples from two different ion-containing polymer systems were used to illustrate the method. In each case, the viscoelastic response was characterized by two relaxation mechanisms; the contributions from each mechanism were separated and two master curves for each polymer were obtained, from which the viscoelastic response at any time and temperature within the range studied could be described. The activation energies corresponding to each mechanism were obtained from an analysis of their respective shift factors.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. M. K. is indebted to the N. R. C. Canada for a 1967 scholarship.

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Nuclear Magnetic Resonance Studies on Microstructure of Ethylene Copolymers. V. 220-MHz Proton Resonance Spectra of Ethylene–Vinyl Chloride Copolymers[1]

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ABSTRACT: 220-MHz proton nmr spectroscopy has been utilized to examine the microstructure of ethylene–vinyl chloride (E–VCl) copolymers. It was found that the monomers are distributed in an ideally random fashion and that the formation of racemic dyads of vinyl chloride units is slightly favored over that of meso dyads during copolymerizations. Moreover, the polyethylene segments of E–VCl polymers, when dissolved in 1-chloronaphthalene solution, undergo intramolecular conformational transitions similar to those observed for ethylene-vinyl ester copolymers.

The high-resolution proton resonance spectra of ethylene-vinyl chloride (E–VCl) copolymers have been investigated by a number of authors. Schaefer[2] showed that 100-MHz nmr spectroscopy when used with spin decoupling provides a powerful tool for determining the chemical and stereochemical sequence distributions in these copolymers. In a systematic study of the 60-MHz copolymer spectra, Wilkes *et al.* have deduced the comonomer dyad distributions and the kinetics of bulk E–VCl polymerizations.[3] A similar nmr method was utilized by Misono and coworkers to elucidate the microstructure of E–VCl copolymers prepared by trialkylboron catalysis.[4]

In the previous papers of this series, we demonstrated that 220-MHz proton nmr spectroscopy is extremely useful for investigating the microstructure of ethylene copolymers. This high radiofrequency (magnetic field) spectroscopic technique has been successfully applied to determine: (1) monomer sequence distributions in ethylene-vinyl formate (E–VF)[5] and ethylene-vinyl acetate (E–VA)[6] polymerizations, (2) complex formation between the segments of E–VA copolymers and the solvent molecules,[7] and (3) intramolecular conformational transitions of the polyethylene sequences of E–VF and E–VA polymers in solution.[1,7] Recently we have extended our studies to include copolymers of ethylene and vinyl chloride. The results of our studies are presented in this paper.

Experimental Section

Ethylene-vinyl chloride (E–VCl) copolymers were prepared by high-pressure free-radical copolymerizations of ethylene ($CH_2{=}CH_2$) and vinyl chloride ($CH_2{=}CHCl$). The conversions

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[1] Part IV: T. K. Wu, *Macromolecules*, **3**, 610 (1970).

[2] J. Schaefer, *J. Phys. Chem.*, **70**, 1975 (1966); eq 3, 4, 5, and 6 are only valid for the terminal model.

[3] C. E. Wilkes, J. C. Westfahl, and R.H. Backderf, *J. Polym. Sci., Part A-1*, **7**, 23 (1969).

[4] A. Misono, Y. Uchida, K. Yamada, and T. Saeki, *Bull. Chem. Soc. Jap.*, **41**, 2995 (1968).

[5] T. K. Wu, *J. Phys. Chem.*, **73**, 1801 (1969).

[6] T. K. Wu, *J. Polym. Sci., Part A-2*, **8**, 167 (1970).

[7] T. K. Wu, *Macromolecules*, **2**, 520 (1969).

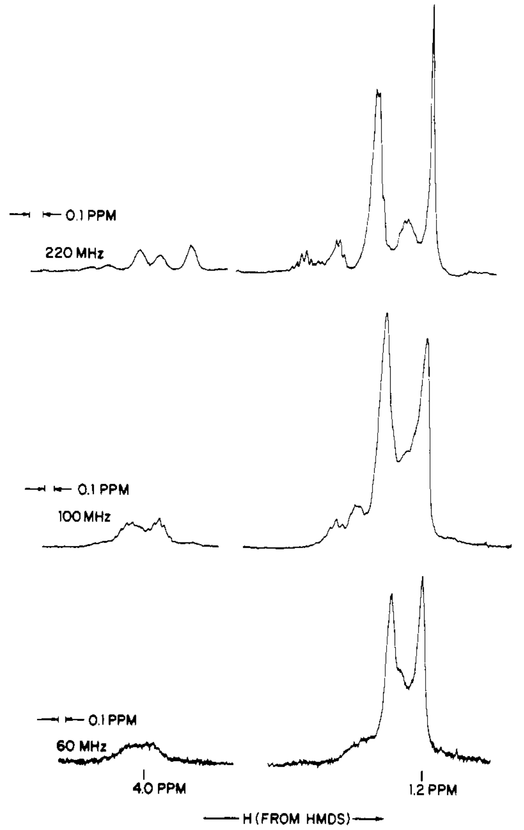

Figure 1. Proton nmr spectra of an E-VCl (mole fraction of VCl = 0.402) at 60, 100, and 220 MHz.

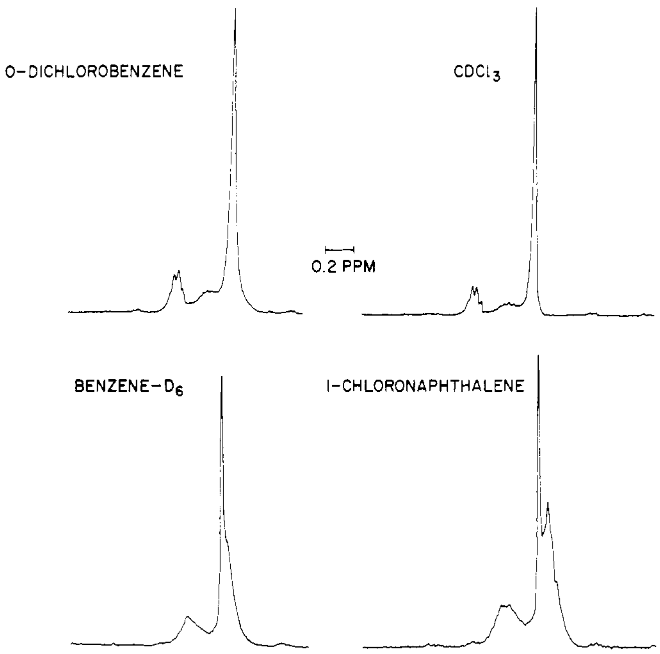

Figure 2. Solvent effects on nmr spectra of methylene protons in an E-VCl copolymer (mole fraction of VCl = 0.185)

were about 10%. Determinations of copolymer compositions were carried out by elemental analyses of carbon, hydrogen, and chlorine. The inherent viscosities of these polymers in chloroform at 30° were greater than 0.4 in all cases.

The proton nmr spectra were obtained on Varian A-60, HA-100, and HR-220 nmr spectrometers. Preparation of the nmr sample solutions and spectral measurements were carried out in accordance with the previously described procedures.[5] The chemical shift values reported in this study were measured with respect to an internal reference, hexamethyldisiloxane.

Table I
Solvent Effects on Proton Chemical Shifts of Ethylene-Vinyl Chloride Copolymers

	Proton Chemical Shift[b]				
Peak[a]	$CDCl_3$	*ortho*-Dichlorobenzene	Pyridine	Benzene	1-Chloronaphthalene
1	1.213	1.199	1.205	1.191, 1.255	1.123, 1.191
2	1.400	1.380	1.400	1.464	1.432
3	1.651	1.600	1.646	1.691	1.659
4	1.918	1.856	1.982	1.809	1.864
5	2.181	2.118	2.236	2.055	2.005
6	3.801	3.754	3.864	3.618	3.659
7	3.996	3.972	4.127	3.905	3.932
8	4.141	4.134	4.250	4.164	4.127
9	4.341	4.350	4.518	4.409	4.368
10	4.477	4.495	4.591	4.518	4.582

[a] See Table II (see peak assignments). [b] Proton chemical shifts (in ppm) were measured with respect to an internal reference, hexamethyldisiloxane. The $CDCl_3$ and benzene solution spectra were obtained at 60°C. For chloroaromatic solvents and pyridine a temperature of 85° was used to record the spectra.

Results and Discussion

Figure 1 depicts the nmr spectra of an E-VCl copolymer obtained at various magnetic field strengths. This copolymer was examined at 60° in deuteriochloroform ($CDCl_3$) solution. It is seen that a substantially greater number of proton resonances of both the methylene and methine groups are resolved in the higher radiofrequency spectra. In fact, the spectral features of this copolymer obtained at 220 MHz are very similar to those of the corresponding 100-MHz double-resonance spectra reported by Schaefer.[2] Thus, it follows that we can readily determine the chemical and stereochemical sequence distributions in E-VCl polymerizations by analyzing the 220-MHz proton spectra.

Our previous studies showed that the effects of solvents can be used to improve the spectral resolution of ethylene copolymers.[5,7] In this work, we have obtained the spectra of E-VCl polymers dissolved in a variety of solvents. Some examples are presented in Figure 2 and the observed proton chemical shifts are summarized in Table I. It is noteworthy that, with the exceptions of benzene and 1-chloronaphthalene, the effects of most solvents on the proton shifts of this copolymer do not show any significant differences. Therefore, based on these results and the solubility characteristics of E-VCl copolymers, we have chosen $CDCl_3$ and orthodichlorobenzene as the solvents for our studies of the monomer sequence distributions.

In Table II are shown the proton chemical shifts of E-VCl polymers. Our spectral assignments were facilitated by examining the previously reported chemical shift data on these copolymers and the related model compounds. Particularly helpful are the published 220-MHz spectra of chlorosulfonated polyethylenes[8] which have many similar monomer sequences. At a high radiofrequency of 220 MHz the spin multiplets of the various proton types in the spectra of E-VCl polymers become clearly recognizable. This, in turn, can be used to aid spectral interpretation. For example, Brame has utilized the spin-splitting pattern to confirm his assignments of methylene and methine proton resonances of chlorosulfonated polyethylenes. In fact, his reported spectra of methylene protons are almost identical with those of the three high-field methylene groups of E-VCl polymers. Examination of the

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(8) E. G. Brame, J., *J. Polym. Sci., Part A-1,* **9,** 2051 (1971).

Table II
Spectral Assignments for Ethylene–Vinyl Chloride Polymers

Chemical Shifts[a]	Proton[b]	Spin Multiplets
1.213	$\mathrm{CH_2CH_2}CH_2CH_2\mathrm{CH_2CH_2}$ $\mathrm{CH_2CH_2}CH_2\mathrm{CH_2CH_2CHCl}$	Singlet
1.400	$\mathrm{CH_2CHClCH_2}CH_2\mathrm{CH_2CHCl}$	Overlapping pentets
1.651	$\mathrm{CH_2CHClCH_2}CH_2\mathrm{CH_2CHCl}$ $\mathrm{CH_2CHCl}CH_2\mathrm{CH_2}$	Quartet
1.918	$\mathrm{CH_2CHCl}CH_2\mathrm{CHCl}$ (racemic)	Triplets
2.181	$\mathrm{CH_2CHCl}CH_2\mathrm{CHCl}$ (meso)	Multiplets
3.801	$\mathrm{CH_2CH_2CH_2}CH\mathrm{ClCH_2CH_2}$	Pentet
3.996	$\mathrm{CH_2CHClCH_2}CH\mathrm{ClCH_2CH_2}$ (meso)	Broad pentet
4.141	$\mathrm{CH_2CHClCH_2}CH\mathrm{ClCH_2CH_2}$ (racemic)	Pentet
4.280	$\mathrm{CH_2CHClCH_2}CH\mathrm{ClCH_2CHCl}$ (isotactic)	Unresolved multiplets
4.341	$\mathrm{CH_2CHClCH_2}CH\mathrm{ClCH_2CHCl}$ (heterotactic)	Broad multiplet
4.477	$\mathrm{CH_2CHClCH_2}CH\mathrm{ClCH_2CHCl}$ (syndiotactic)	Broad multiplet

[a] Chemical shifts were derived from the spectra obtained in $\mathrm{CDCl_3}$ solution at 60°. [b] The protons of interest are in italic type.

Table III
Nmr Peak Intensities and Monomer Distribution Parameters of Ethylene–Vinyl Chloride Copolymers

	Peak Intensity[a]			Addition Probabilities[b]				
Mole Fraction of VCl	VVV	VVE	EVE	P_{VVE}	P_{EVV}	P_{VEE}	$\langle V\rangle_{\mathrm{obsd}}$[c]	$\langle V\rangle_{\mathrm{ir}}$[c]
0.433	0.198	0.518	0.284	0.568	0.477	0.564	1.84	1.76
0.402	0.186	0.512	0.302	0.579	0.459	0.611	1.79	1.67
0.292	0.077	0.378	0.545	0.710	0.258	0.717	1.36	1.41
0.185	0.034	0.261	0.705	0.79	0.16	0.82	1.20	1.23
0.116	0.014	0.189	0.797	0.87	0.11	0.89	1.12	1.13

[a] Peak intensities of methine protons were normalized. The designation, VVV, represents a triad of VCl–VCl–VCl, VVE, and EVE can be defined analogously. [b] P's are the various addition probabilities described by the subscripts. [c] $\langle V\rangle$ is the number-average sequence length of VCl monomer. Obsd is derived from the observed spectra by using eq 6 and ir is calculated from ideally random distribution (eq 7).

spectra illustrated in Figure 3 reveals that the two overlapping triplets centered at 1.92 ppm arise from the two homosteric methylene groups of mrm and rrr tetrads of VCl sequences as in the case of poly(vinyl chloride). The multiplets centered at 2.18 ppm can similarly be assigned to the mmm, mmr, and rmr tetrads.[9] Moreover, in the methine proton region the quintet at 3.8 ppm is due to the VCl units in E-VCl-E triads, in which the methine protons are coupled to four magnetically equivalent methylene protors. The broadening of this quintet in the spectrum of the copolymer of higher VCl content probably arises from the combined contributions of the pentads E-E-VCl-E-E, VCl-E-VCl-E-E, and VCl-E-VCl-E-VCl.

From the double resonance spectra of E-VCl polymers, Schaefer was able to derive the various addition probabilities which were then used to describe the comonomer sequence distributions and copolymerization kinetics.[2a] The equations used are as follows

$$P_{\mathrm{VVE}} = 1/(1 + 2I_{\mathrm{VVV}}/I_{\mathrm{VVE}}) \quad (1)$$

$$P_{\mathrm{EVV}} = 1/(1 + 2I_{\mathrm{EVE}}/I_{\mathrm{VVE}}) \quad (2)$$

$$P_{\mathrm{EEV}} = P_{\mathrm{VVE}}f_{\mathrm{V}}/(1 - f_{\mathrm{V}}) \quad (3)$$

$$P_{\mathrm{VEE}} = 1 - P_{\mathrm{VEV}} \quad (4)$$

where P_{VVE} represents the probability that a growing polymer chain ending in VCl-VCl will add an E unit. P_{EVV}, P_{EEV}, and P_{VEE} are defined in an analogous manner. I's are the methine proton peak intensities of the triads indicated by the subscripts and f_{V} is the mole fraction of VCl in the copolymer. The average sequence lengths of ethylene and vinyl chloride units, $\langle E\rangle$ and $\langle V\rangle$, can also be calculated by

$$\langle E\rangle = 1 + P_{\mathrm{VEE}}/P_{\mathrm{EEV}} \quad (5)$$

$$\langle V\rangle = 1 + P_{\mathrm{EVV}}/P_{\mathrm{VVE}} \quad (6)$$

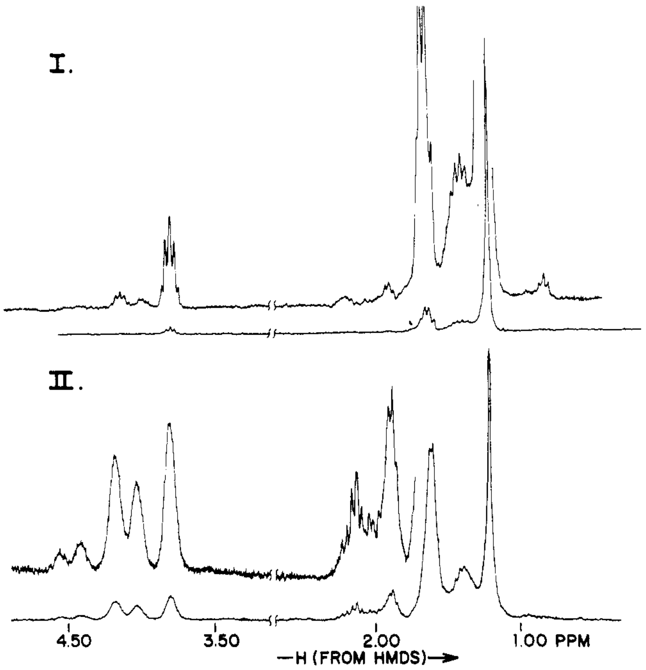

Figure 3. 220-MHz spectra of E–VCl copolymers in $\mathrm{CDCl_3}$ solution. Mole fractions of VCl: of the upper = 0.116, the lower = 0.433.

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[9] F. Heatley and F. A. Bovey, *Macromolecules*, **2**, 241 (1969). m and r designate, respectively, meso and racemic dyads of vinyl chloride units.

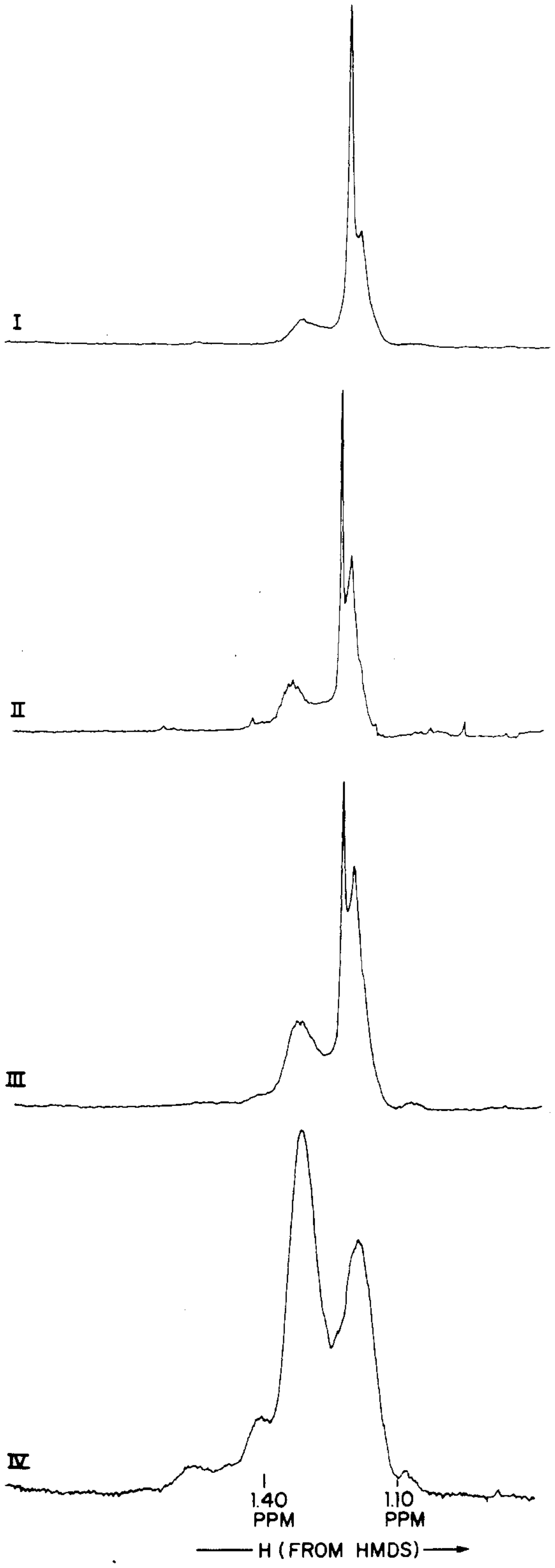

Figure 4. 220-MHz 1-chloronaphthalene solution spectra in the methylene proton region of several E-VCl copolymers. Mole fractions of ethylene: of I = 0.884, II = 0.815, III = 0.708, IV = 0.598.

Table IV
Stereochemical Sequence Distributions in Ethylene-Vinyl Chloride Copolymers

	VCl-VCl Dyads[a]	
Mole Fraction of VCl	Racemic	Meso
0.433	a. 0.53	0.47
	b. 0.60	0.40
0.402	a. 0.57	0.43
	b. 0.58	0.42
0.292	a. 0.50	0.50
0.185	a. 0.55	0.45
0.116	a. 0.54	0.46

[a] a and b designate, respectively, the measurements from methine and methylene proton resonances.

Because P_{VEE} was found to be equal, within experimental errors, to P_{VVE} and P_{EVE} for all the copolymers samples examined, he concluded that monomer sequence distributions in E-VCl polymerizations are ideally random. Subsequently, Wilkes and coworkers[3] have carried out a systematic study of the 60-MHz copolymer spectra and the composition data of E-VCl polymerizations. They found that ethylene and vinyl chloride do not copolymerize randomly but that the order of addition of monomer to a growing E-VCl polymer chain is dependent on the nature of its terminal unit.

In Table III are summarized the normalized methine proton peak intensities of VCl units, which are, in fact, the fractions of the VCl triads in the copolymers. Because of the overlap in the methylene region, we have not attempted quantitative measurements of the proton resonances. However, by using our data on the methine protons and eq 1-5, we have calculated the various addition probabilities and the average sequence lengths of monomers (see Table III). It is interesting to note that $P_{\mathrm{VVE}} = P_{\mathrm{VEE}}$ and $P_{\mathrm{VEE}} = 1 - P_{\mathrm{EVV}}$ within the experimental errors of about ±5% in all cases. This means that the addition probabilities are not dependent on the nature of the terminal units or of the penultimate monomer units in the growing chains. In other words, copolymerizations of ethylene and vinyl chloride are statistically random.

In an ideally random copolymer, the average sequence length of one comonomer can be directly calculated from its composition,[5] *i.e.*

$$\langle V \rangle_{\mathrm{i.r}} = 1/f_{\mathrm{E}} \qquad (7)$$

In the last two columns of Table III we have compared the average sequence lengths obtained from the methine proton resonances with the corresponding calculated values based on eq 7. The fact that the observed and calculated $\langle V \rangle$ values agree reasonably well provides further supporting evidence to our conclusion that E-VCl polymerizations can be described by a Bernoullian (zeroth-order Markoffian) process.

The stereochemical sequence distributions of VCl units can be readily determined from the 220-MHz spectra of E-VCl copolymers. For example, the methylene proton resonances at about 2.0 ppm can perhaps yield information on the tacticity of VCl units in terms of tetrad distributions. However, since there is presently no independent evidence available to distinguish the methylene groups situated in VVVV tetrads from those situated in EVVV or EVVE comonomer tetrads, we have used these methylene proton peaks to measure only the stereochemical dyads of VCl units in the copolymers. In addition, because of the relatively low VCl contents in the polymers used in this study, the methine proton resonances due to VVV triads were not frequently observed. Nevertheless, from the two multiplets of VVE triads the stereochemistry of VCl comonomers can be derived to complement the measurements obtained from the methylene proton spectra. The results in Table IV indicate that formation of racemic dyads of VCl is somewhat slightly preferred to that of meso dyads during E-VCl copolymerizations.

Previously we have found that the polyethylene segments of ethylene–vinyl ester copolymers undergo intramolecular conformational transitions in solution.[1,7] More specifically, we have identified the doubled alkanelike methylene proton peaks in the aromatic solution spectra of E–VF and E–VA copolymers as the two types of intramolecular structures, "monomeric" and "polymeric" species of the ethylene sequences. The polymeric species probably arises from intramolecular chain folding of the polyethylene segments containing 8 or more ethylene units. In addition, the existence of the polymeric structure in these copolymers appears to depend on their compositions and, to a lesser extent, on the monomer sequence distributions. It is seen that in Figure 2 the resonance peak due to the alkane-like methylene proton groups (at 1.2 ppm) is further split into two lines in the 1-chloronaphthalene solution spectrum. The spectral feature of the doubled alkanelike methylene proton resonances, which consists of a sharp line at lower field and a broad peak at higher field, is remarkably similar to those observed for E–VA and E–VF copolymers. The sharp methylene peak was then assigned to the equivalent internal methylene groups in the polymeric polyethylene sequences and the broad upfield resonances to the disordered monomeric methylene groups in accordance with our previous work.

In order to examine the effects of copolymer composition on the intramolecular structure formation we have obtained the 1-chloronaphthalene solution spectra of several E–VCl polymers. (see Figure 4). As in the cases of ethylene–vinyl ester copolymers,[1,7] the spectra of the doubled alkane-like methylene protons are indeed dependent on the comonomer (VCl) contents in the polymers. Particularly noteworthy is the fact that in the spectrum of an E–VCl polymer containing 43.3 mol % of VCl the feature of the alkane-like methylene proton resonances is significantly altered. This is consistent with the previous observation that the fraction of ethylene in blocks of 8 or more ethylene units of a statistically random copolymer containing more than 37.5 mol % of comonomer becomes negligibly small and the formation of polymeric structure by intramolecular chain folding is precluded.[7] As implied by our earlier work the results of the present study lead to an important conclusion that the intramolecular conformational transitions observed in the nmr spectra of ethylene copolymers arise from the polyethylene segments and are not affected by the nature of the comonomer units.

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Dilute Solution Behavior of Polyelectrolytes. Potentiometric Titration Studies on Chain Conformation

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ABSTRACT: Potentiometric and viscometric studies of copoly(ethyl acrylate–acrylic acid) were made in a mixed isopropyl alcohol–water (4:1) medium as a function of ionic strength. Potentiometric titrations resulted in distinct conformational transition curves similar to those observed for poly(methacrylic acid) and poly(glutamic acid). The transition is most pronounced in the absence of salt. It is believed that our copolymer goes through a transition from a compact globular coil at a low degree of ionization to a more extended coil at a high degree of ionization. The free-energy change for the conformational transition of the un-ionized molecule estimated from the empirical Henderson–Hasselbalch extrapolations is approximately in the range of 60–90 cal/mol. In addition, the titration behavior of three copolymers of the same chain length but different acid contents was compared. The data suggest that the start of the transition region occurs at a lower degree of ionization for chains with higher acid content. However, the fraction of charge per residue at the onset of the transition is about 0.10 for the three copolymers studied.

Light-scattering and intrinsic-viscosity studies of several fractions of copoly(ethyl acrylate–acrylic acid) (mole ratio 3:1) in organic solvents and in aqueous NaCl solutions as a function of ionic strength, C_s, have been reported previously.[1] Data on radius of gyration, second virial coefficient, and intrinsic viscosity as a function of ionic strength (see Figure 1a–c for data on one fraction, F4) suggest that the polymer goes through a conformational transition from an extended coil at low C_s to a compact globular coil at high C_s. In the low C_s region below 0.1 *N* NaCl, the coil becomes more compact possibly attributed charged groups. In the presence of a moderate concentration of NaCl, the screening effect of the counterions tends to diminish the repulsive forces and the size of the coil becomes smaller. At high ionic strength above 0.5 *N* NaCl, the coil becomes more compact possibly attributed to both the further reduction in repulsive forces and the increasing intramolecular hydrophobic attraction of the ester groups along the chain.

The possibility of creating and stabilizing a compact form of the molecule by interaction of polymer side-chain groups has prompted further study of the conformational transition of this copolymer. Potentiometric titration of the polyacid was selected as the tool to investigate this molecular behavior. This type of study has proved to be very helpful in identifying helix–coil transitions in polypeptides such as poly(glutamic acid) (PGA)[2-5] and poly-

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