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Carbon-13 Nuclear Magnetic Resonance Characterization of Random Ethylene–Vinyl Chloride Copolymers

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ABSTRACT: A complete series of ethylene–vinyl chloride (E–V) copolymers have been prepared by reductive dechlorination of poly(vinyl chloride) (PVC) with tri-*n*-butyltin hydride. ^{13}C NMR was employed to determine the microstructure of each E–V copolymer including the overall comonomer composition and sequence and the stereosequence of neighboring vinyl chloride (V) units. Our detailed analysis of E–V microstructure by ^{13}C NMR was made possible by comparison of the observed spectra with the ^{13}C NMR chemical shifts previously calculated for these copolymers based on γ-gauche shielding effects. Dechlorination was found to be an approximately random process in terms of comonomer sequence; however, VV dyads with a meso stereosequence were found to be significantly more susceptible to dechlorination than racemic VV dyads. GPC determination of molecular weights revealed that the reductive dechlorination of PVC to yield E–V copolymer does not result in chain scission or cross-linking. Consequently, we have produced a series of E–V copolymers with nearly the same chain lengths as the starting PVC, each with a well-characterized microstructure.

Introduction

Recently considerable effort has been applied to the study of poly(vinyl chloride) (PVC) microstructure.[1] A key step in much of this work is the reductive dechlorination of PVC to polyethylene (PE) with tri-*n*-butyltin hydride (Bu_3SnH). The structure of the starting PVC is then deduced from that of the resulting PE, principally by ^{13}C NMR analysis.

It is also possible to obtain ethylene–vinyl chloride (E–V) copolymers by the incomplete reduction of PVC.[2] A series of ethylene–vinyl bromide copolymers have already been obtained by Cais and Kometani[3] through the Bu_3SnH reductive debromination of poly(vinyl bromide).

Traditional means of obtaining E–V copolymers suffer from several shortcomings. Chlorination of PE[4] results in head-to-head (vicinal) and multiple (geminal) chlorination leading to structures which are not characteristics of E–V copolymers. Direct copolymerization of E and V monomers does not usually lead to random E–V copolymers covering the entire range of comonomer composition. Free-radical copolymerization[5,6] at low pressures yields E–V copolymers with V contents from 60 to 100 mol %. γ-Ray-induced copolymerization[7] under high pressure yields E–V copolymers with increased amounts of E, but it appears difficult to achieve degrees of E incorporation greater than 60 mol %.

Several factors serve to motivate our interest in E–V copolymers. First is the convenient means for obtaining these copolymers provided by the Bu_3SnH reduction of PVC. Second, our ability to assign the ^{13}C NMR spectra of E–V copolymers[8] means we can determine the details of their microstructure. Third, our interest in using electrical birefringence measurements (Kerr effect)[9-11] performed on dilute polymer solutions to characterize their structures and conformations prompts us to consider the Kerr effect study of the E–V system, because ^{13}C NMR provides us with an independent means to determine both of these characteristics. Fourth, we would like to measure several solid-state properties[2] of a well-characterized copolymer system with the view of eventually establishing structure–property relations.

In this paper we outline the preparation and characterization of E–V copolymers. Their physical properties, measured both in dilute solution and in the solid state, will be discussed in subsequent contributions.

Experimental Section

Preparation of E–V Copolymers. PVC obtained from Aldrich (No. 18958-8) was dissolved in tetrahydrofuran (THF) that had been passed through basic alumina. The PVC was next precipitated from cold methanol, filtered, and dried in a vacuum oven overnight at ambient temperature.

[†] Merck & Co., Inc., Rahway, NJ.

Reductions[1,3] of the clean PVC by Bu_3SnH (Alfa Products, Ventron Division) were conducted under dry nitrogen atmosphere in THF which had been passed through basic alumina. Overnight reductions at 60 °C with refluxing were achieved with about 20% excess Bu_3SnH over the amount calculated for the desired level of dechlorination. For the higher levels of reduction it was necessary to recharge the reaction mixture with AIBN and continue refluxing.

After cooling, the completed reaction mixture was added dropwise to hot *n*-hexane with stirring. The resultant E–V copolymer was isolated by centrifugation at 50 °C from the hot *n*-hexane and dried overnight in a vacuum oven at ambient temperature.

Whenever a precise level of dechlorination was desired, small aliquots of the reaction mixture were removed periodically and analyzed by ^1H NMR to obtain comonomer composition. The reaction was stopped as soon as the ^1H NMR analysis indicated achievement of the desired level of reduction.

Molecular Weights. Molecular weights were measured for the starting PVC and two E–V copolymers (E-V-84 and E-V-14) by gel permeation chromatography (GPC). GPC analyses for PVC and E-V-84 were performed in THF at 25 °C by using a polystyrene calibration of elution volume and molecular weight. E-V-14 was measured in 2,4,6-trichlorobenzene at 135 °C with a polyethylene calibration of elution volume and molecular weight.

^{13}C NMR Measurements. The 50.31-MHz ^{13}C NMR spectra of the ethylene–vinyl chloride copolymers were recorded on a Varian XL-200 NMR spectrometer by using 18% (w/v) solutions in a 4:1 mixture of 1,2,4-trichlorobenzene/*p*-dioxane-d_8. Hexamethyldisiloxane (HMDS) was used as an internal reference (2.0 ppm vs. Me_4Si). The observing temperature was 110 °C. Depending on the extent of reduction, between 2000 and 30 000 scans were required for each spectrum. In all measurements broad-band complete decoupling was used, the pulse angle was 90°, and the free induction decay was stored in 32K computer locations, using a spectral window of 8000 Hz.

In order to obtain quantitative information from the spectra the delay between sampling pulses was varied between 2.0 and 10.0 s. The shorter values were used for PVC and samples with low levels of reduction. For these samples the ^{13}C spin–lattice relaxation times (T_1) are all less than 0.4 s.[12] The longer pulse intervals were used for the highly reduced samples where the ^{13}C T_1 values are less than 2.0 s.[13]

Results and Discussion

The ^{13}C NMR spectra of PVC and several E–V copolymers are shown in Figure 1a–c. The assignments of the methine (1-centered) and methylene (0-centered) resonances were made on the basis of the ^{13}C chemical shifts previously[8] calculated for E–V copolymers via the γ-gauche effect method.[14] Since the PVC homopolymer contains alternating 0's and 1's (methylene and methine carbons, respectively), the 1's which remain in the E–V copolymer following removal of chlorine by Bu_3SnH reduction must be separated by an odd number of 0's. This assumes, of course, a regular head-to-tail chain in the starting PVC. Our earlier ^{13}C NMR studies on PVC support this assumption.[1]

The methine carbon region (56–64 ppm) is divided into three groups of resonances depending upon whether the observed carbon sees zero, one, or two chlorine atoms three bonds removed. The further splittings within each region are the result of differences in chlorine atom placement more than three bonds from the observed carbon and also differences in the stereochemistry along the chain.

The methylene carbon resonances are also divided into three regions, centered at 27, 38, and 47 ppm, depending upon whether the observed methylene carbon has zero, one, or two β-chlorine substituents. A further splitting is observed within the upfield 000-centered sequences, which again is dependent upon the number of chlorine atoms three bonds removed from the observed methylene carbon. A similar observation for the methylene carbon resonances has been reported for ethylene–vinyl bromide copolymers.[3] As with the methine resonances, the smaller splittings observed within each methylene region are due to different stereosequences and sensitivity to chlorine atom placement four or more bonds removed from the observed carbon. It should also be noted that the differences in chemical shift position for sequences in Figure 1b as compared to the same sequences in Figure 1c are also due to chlorine atom placements more than three bonds from the observed carbon.

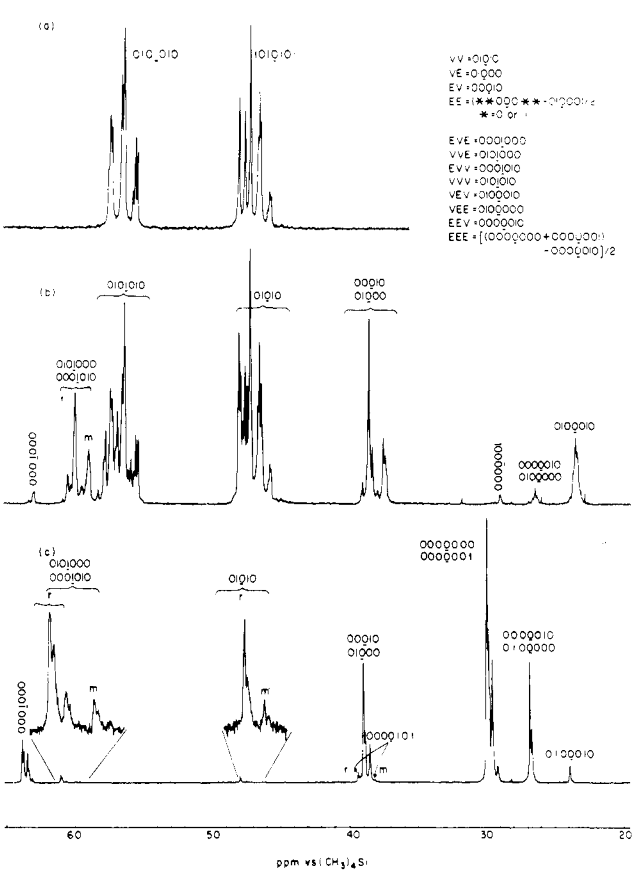

Figure 1. 50.31-MHz ^{13}C NMR spectra of PVC (a) and two partially reduced PVC's, E-V-84 (b) and E-V-21 (c). Please note the table of E–V microstructural designations in the upper right-hand corner of the figure, where 0,1 ≡ CH_2, CHCl carbons. Resonances correspond to underlined carbons. The assignment of the different stereosequences is given in ref 8 and 12.

In order to analyze the copolymers in terms of comonomer compositions, it is necessary to relate each comonomer dyad and triad sequence to the appropriate combination of NMR observable sequences as assigned in Figure 1. The dyad sequences can be measured most easily from the methylene or 0-centered resonances. It can be shown that the VV dyad is represented by the 01010 resonance. The sequences 00010 and 01000 represent the EV and VE dyads, respectively, and are not distinguishable by NMR. However, the probability of an EV dyad must necessarily equal that of the VE dyad. Therefore, each is measured by determining one-half the integral area of the resonances at ~38 ppm. The 000-centered sequences between 23 and 30 ppm represent the dyads EE + $^1/_2$VE + $^1/_2$EV or just EE + VE. Therefore, we can obtain a measure of EE by summing the 000-centered resonances, subtracting one-half of the 00010 + 01000 resonances to remove the VE and EV contribution, and finally dividing the result by 2. The division by 2 results from the fact that the EE dyad generates two methylene carbon resonances in this upfield region, while the VE and EV dyads generate

Table I
Composition of E–V Copolymers

	X_V, mol % vinyl chloride units					
copolymer	*a*	*b*	*c*	*d*	$\bar{N}_V$[e]	$\bar{N}_E$[e]
E–V-85	83.5	86.5	85.9	85.3	6.8	1.1
E–V-84	84.3	84.3	84.4	84.3	6.4	1.2
E–V-71	70.5	70.9	70.6	70.7	3.0	1.3
E–V-62	64.0	62.3	60.5	62.3	2.2	1.4
E–V-61	62.4	60.1	57.7	61.5	2.3	1.5
E–V-60	63.4	61.8	59.4	60.1	2.1	1.4
E–V-50	50.5	49.8	50.1	50.1	1.6	1.6
E–V-46	47.2	45.6	44.1	45.6	1.5	1.8
E–V-37	38.5	37.2	36.2	37.3	1.3	2.2
E–V-35	37.0	33.9	33.5	34.8	1.3	2.5
E–V-21	22.2	21.0	20.5	21.2	1.1	4.1
E–V-14	10.6	12.7	17.4	13.6	1.0	6.0
E–V-2	2.1	2.5	2.7	2.4	1.0	38.3

[a] Obtained from eq 1. [b] Obtained from eq 2. [c] Obtained from eq 3. [d] Average monomer composition. [e] Average of dyad and triad analyses.

one resonance in the 27 ppm region and one resonance in the 38 ppm region. The VV dyad produces only one methylene resonance, which is at ~47 ppm. Since our measurement of the VV, VE, and EV dyads involves counting only one carbon per dyad, we therefore must also count the EE dyad with only one carbon per dyad.

At the triad level there are eight comonomer sequences. Since NMR cannot distinguish chain direction, VEE is not observably different from EEV, and similarly, VVE is not distinguished from EVV. However, these pairs of triads must be equal in probability, i.e., VEE = EEV and VVE = EVV. The most direct measure of triad sequences is from the methine carbon resonances in the 56–64 ppm region and the upfield methylene carbon resonances from 24–30 ppm. The EVE triad is measured by $000\underline{1}000$ at ~63.5 ppm. Since VVE must equal EVV, each is equal to one-half the integral sum of the $010\underline{1}000$ and $000\underline{1}010$ resonances at ~60 ppm. The VVV triad is represented by the $010\underline{1}010$ sequences at 56–59 ppm. The VEV sequence is measured by the $010\underline{0}010$ resonances at ~24 ppm. As indicated above, VEE must equal EEV, and each is measured as one-half the integral sum of the $010\underline{0}000$ and $000\underline{0}010$ resonances at ~27 ppm. The EEE triad is counted twice by the methylene resonances at ~30 ppm. In addition, the contribution of the EEV triad represented by $000\underline{0}001$ must be removed from the signals at ~30 ppm. Therefore, EEE is determined by integrating the resonances at ~30 ppm, subtracting the measure of EEV as mentioned above, and dividing the result by 2. In this manner a quantitative measure of each dyad and triad comonomer sequence is obtained for the E–V copolymers. A summary of the relationships between these comonomer sequences and the NMR observable resonances is given in Figure 1. For a thorough study of sequence probabilities the reader is directed to the work of Cais and Sloane[15] in which a detailed analysis of sequence statistics for regular head-to-tail chains, as well as chains containing head-to-head junctions, is presented.

A list of all E–V copolymers prepared in the present study are presented in Table I together with their overall comonomer compositions. For each chlorine atom removed in the Bu_3SnH reduction of PVC a methine carbon is converted into a methylene carbon (compare parts a–c of Figure 1). Thus, the mole percent vinyl chloride units, X_V, in an E–V copolymer may be obtained from the ratio of ^{13}C NMR resonance areas

$$X_V = 100[2I_{CH}/(I_{CH} + I_{CH_2})] \qquad (1)$$

where I_{CH} and I_{CH_2} are the integrals of the resonances in the methine ($\underline{1}$) and methylene ($\underline{0}$) carbon regions of the ^{13}C NMR spectra, respectively (see Figure 1b and Table I, column 2).

The dyads and triads, as defined above in terms of 0's and 1's, are tabulated in Figure 1. Overall monomer compositions may be determined[16] from the dyad and triad probabilities, P_{xy} and P_{xyz}, where x,y,z = V or E, according to

$$X_V^D = 100[P_{VV} + \tfrac{1}{2}(P_{VE} + P_{EV})] \qquad (2)$$

$$X_V^T = 100[P_{VVV} + P_{EVE} + P_{VVE} + P_{EVV}] \qquad (3)$$

X_V^D and X_V^T are the mole percent V units in the E–V copolymers obtained from observed dyad and triad integrals, respectively, and are presented in the third and fourth columns of Table I. Dyad and triad probabilities are listed for each E–V copolymer in Table II. The average monomer composition is presented in the fifth column of Table I.

It is possible from the dyad and triad probabilities to obtain average monomer sequence lengths.[16] As an example

$$\bar{N}_V = \frac{(P_{VV} + P_{VE})}{P_{VE}} \qquad (4)$$

$$\bar{N}_V = \frac{P_{VVV} + P_{EVE} + P_{VVE} + P_{EVV}}{P_{EVE} + P_{VVE}} \qquad (5)$$

where $\bar{N}_V$ is the average length of V sequences. $\bar{N}_V$ and $\bar{N}_E$ calculated from dyad and triad probabilities are presented in the final two columns of Table I.

In Table III we present a comparison of the observed comonomer dyad and triad fractions with those calculated by assuming a completely random or Bernoullian distribution of comonomer units for several E–V copolymers. For lightly reduced E–V copolymers, such as E–V-84, the observed distribution or sequence of comonomer units is

Table II
Dyad and Triad Probabilities of E–V Copolymers

copolymer	P_{VV}	$P_{VE} = P_{VE}$	P_{EE}	P_{EVE}	$P_{VVE} = P_{EVV}$	P_{VVV}	P_{VEV}	$P_{VEE} = P_{EEV}$	P_{EEE}
E–V-85	0.742	0.124	0.011	0.015	0.115	0.619	0.114	0.011	0.0
E–V-84	0.709	0.134	0.023	0.025	0.108	0.615	0.101	0.019	0.004
E–V-71	0.470	0.239	0.052	0.063	0.175	0.310	0.175	0.048	0.008
E–V-62	0.344	0.278	0.099	0.116	0.177	0.177	0.177	0.075	0.027
E–V-61	0.343	0.275	0.107	0.121	0.173	0.198	0.141	0.083	0.029
E–V-60	0.316	0.285	0.114	0.141	0.167	0.154	0.179	0.077	0.038
E–V-50	0.200	0.297	0.205	0.192	0.133	0.073	0.166	0.129	0.045
E–V-46	0.147	0.309	0.235	0.205	0.116	0.037	0.149	0.140	0.098
E–V-37	0.087	0.286	0.342	0.219	0.078	0.012	0.115	0.158	0.183
E–V-35	0.061	0.278	0.383	0.224	0.064	0.015	0.090	0.168	0.208
E–V-21	0.014	0.197	0.593	0.190	0.016	0.0	0.035	0.153	0.436
E–V-14	0.0	0.127	0.746	0.104	0.0	0.0	0.051	0.123	0.599
E–V-2	0.0	0.025	0.950	0.021	0.0	0.0	0.0	0.026	0.926

Table III
Comparison of Observed Dyad and Triad Fractions with Those Calculated for a Random or Bernoullian Distribution of Comonomers

		dyad fractions			triad fractions					
copolymer	X_V	VV	VE + EV	EE	VVV	VVE + EVV	VEV	VEE + EEV	EVE	EEE
E–V-84	84.3	0.709[a]	0.268	0.023	0.615	0.216	0.101	0.038	0.025	0.004
		0.711[b]	0.266	0.023	0.599	0.223	0.111	0.042	0.021	0.004
E–V-62	62.3	0.344	0.556	0.100	0.177	0.354	0.177	0.150	0.116	0.027
		0.388	0.470	0.142	0.242	0.292	0.146	0.177	0.089	0.054
E–V-46	45.6	0.147	0.618	0.235	0.037	0.231	0.149	0.280	0.205	0.098
		0.208	0.496	0.296	0.095	0.226	0.113	0.270	0.135	0.161
E–V-21	21.2	0.014	0.394	0.592	0.000	0.032	0.035	0.306	0.191	0.436
		0.045	0.334	0.621	0.010	0.071	0.035	0.263	0.132	0.489
E–V-14	13.6	0.000	0.254	0.746	0.000	0.000	0.051	0.246	0.104	0.599
		0.018	0.236	0.746	0.003	0.032	0.016	0.203	0.101	0.645

[a] Observed. [b] Random or Bernoullian.

nearly random or Bernoullian. However, as the reduction proceeds, it becomes apparent from the observed dyad and triad fractions that chlorines belonging to V units adjoined by other V units are preferentially removed relative to those adjacent to E units. This results in a decrease in the number of all V and all E runs from a random distribution and leads to an enhanced alternation of E and V units as reflected by the greater than expected amounts of EVE and VEV triads.

Somewhere between 80% and 85% reduction all VV dyads are removed, and all V units are flanked by at least one E unit on both sides. This greater than random isolation of V units tends to reduce the average length of all V and E runs. As an example, for E–V-46 the observed $\bar{N}_V$ and $\bar{N}_E$ (Table I) are 1.5 and 1.8, while those expected for a random 45.6:54.4 (V:E) copolymer are 1.9 and 2.2. The tendency away from randomness, which reduces the blockiness and enhances the alternation of comonomer units in our E–V copolymers, may depress the crystallization[2] of E units, thereby affecting their physical properties.

In addition, comparison of dyad and triad concentrations led to the conclusion that the distributions of comonomer units in our E–V copolymers also do not conform to first-order Markovian statistics.

In part c of Figure 1 the ^{13}C NMR spectrum of E–V-21 is presented together with the microstructural assignment of resonances based on comparisons with chemical shifts calculated[8] via the γ-gauche effect method and to the spectra of chlorinated *n*-alkane model compounds.[17] The methine carbon in the central V unit of the VVE and EVV ($010\underline{1}000$ and $000\underline{1}010$) triads shows two groups of resonances centered at 60.4 ppm which corresponded to r- and m-VV dyads. On the basis of the observation[17] that the methine carbons in *meso*-2,4-dichloropentane and *meso*-4,6-dichlorononane resonate ~1 ppm upfield from their racemic isomers, in agreement with their calculated[8] γ-gauche effect chemical shifts, we assign the upfield resonances to m-(VVE + EVV) triads and the more intense downfield resonances to r-(VVE + EVV) triads.

The resonances between 47.4 and 48.0 ppm correspond to the methylene carbons surrounded by methine carbons in VV ($01\underline{0}10$) dyads with the upfield peak assigned to the m-VV dyad and the downfield peak to the r dyad again in agreement with the order of resonances observed in the dichloroalkanes. As expected, the integral area of the VV methylene carbon resonances are half the area of the methine resonances in VVE plus EVV triads, and the ratio of racemic to meso intensities is the same (4.2) in both regions.

The most downfield and upfield of the methylene resonances in the region 37.8–39.5 ppm are assigned to the methylene carbons adjacent to r- and m-VV dyads, respectively, in the EVV ($000\underline{0}101$) triads. Their partial overlap with resonances from the methylene carbons adjacent to isolated V methine carbons in the $00\underline{0}10$ and $01\underline{0}00$ sequences precludes a quantitative measure of r to m dyads from their intensities.

Table IV
VV Dyad Stereosequence Composition of E–V Copolymers

E–V copolymer	Cl removed, mol %	r/m[a]	k_m/k_r
PVC	0	1.27	
E–V-46	54.4	1.9	1.21
E–V-37	62.7	2.8	1.38
E–V-35	65.2	2.8	1.32
E–V-21	78.8	4.2	1.33
E–V-2[b]	98.1	11.1	1.48

[a] Racemic/meso ratio. [b] Obtained through $LiAlH_4$ reduction by Starnes et al.[18]

The unreduced PVC is a Bernoullian polymer with $P_r = 0.56$ and, therefore, a ratio of r to m dyads of 0.56/0.44 = 1.27 (see Figure 1a). Removal of 79% of the chlorine atoms by Bu_3SnH reduction results in E–V-21 copolymer with an r to m dyad ratio of 4.2. Clearly m dyads are preferentially reduced by Bu_3SnH as was found previously[18] in the $LiAlH_4$ reduction of PVC. In $LiAlH_4$ reductions of PVC, isolated VV dyads were observed[18] even after 98% of the chlorines were removed. For Bu_3SnH-reduced PVC, VV dyads disappear between 80% and 85% removal of chlorine. Consequently, isolated VV dyads are more readily reduced by Bu_3SnH than by $LiAlH_4$.

In Table IV we have presented the observed ratios of r to m dyads as a function of the degree of reduction (mole percent chlorine removed) for the starting PVC and five E–V copolymers (four obtained here by Bu_3SnH reduction and one previously reduced PVC obtained by Starnes et al.[18] through reduction with $LiAlH_4$). As noted by Starnes et al.,[18] we can obtain the ratio of rate constants (k_m/k_r) governing the reduction of m and r dyads by comparing the concentrations of m and r dyads observed in the starting PVC with those remaining in the E–V copolymer. For the four Bu_3SnH-reduced E–V copolymers $k_m/k_r = 1.31 \pm 0.1$, while for $LiAlH_4$-produced E–V, Starnes et al.[18] found a similar value $k_m/k_r = 1.48$.

It would appear that the ratio of rate constants governing the reduction of m and r dyads is independent of the degree of reduction. Apparently the relative rates of chlorine removal from m and r dyads is independent of longer-range E–V microstructure, such as which particular parent triad contains the VV dyad. In a subsequent publication we plan to discuss more fully the mechanistic features of the reductive dechlorination of PVC. This

Table V
Molecular Weights of PVC and E–V Copolymers

	M_n		M_w		
polymer	obsd[a]	calcd[b]	obsd[a]	calcd[b]	M_w/M_n
PVC	58000		106000		1.8
E-V-84	50000	53000	109000	97000	2.2
E-V-14	26000	30000	38000	55000	1.5

[a] GPC. [b] Expected from chlorine loss.

discussion should be facilitated by comparison of the microstructures of additional E–V copolymers obtained both by Bu_3SnH and $LiAlH_4$ reduction and also by examining the products resulting from the reduction of PVC oligomers.

Table V presents the results of our GPC analyses of the molecular weights of our starting PVC and two E–V copolymers obtained by reductive dechlorination of PVC with Bu_3SnH. Comparison of the molecular weights expected from loss of chlorine with those measured by GPC for E–V-84 and E–V-14 indicate that Bu_3SnH reduction of PVC does not produce significant chain scission or cross-linking. Instead, our initial PVC containing a number average of ~1000 repeat units has been converted to a series of E–V copolymers each of ~1000 repeat units.

Reductive dechlorination of PVC with Bu_3SnH has produced a series of E–V copolymers each with the same chain length as the starting PVC, but with differing amounts of pendant chlorine atoms. Detailed ^{13}C NMR analysis, which was materially assisted by chemical shifts calculated[8] by the γ-gauche effect method,[14] has revealed the overall comonomer composition, comonomer sequence distribution, and the stereoregularity of the vinyl chloride sequences. Thus, we have a well-characterized copolymer system upon which we are proceeding to measure physical properties in the hope of eventually being able to establish structure–property relations.

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Multinuclear Magnetic Relaxation Studies of Aqueous Poly(ethylene oxide) Solutions Containing Alkali Halides

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ABSTRACT: The nuclear magnetic relaxation rates of ^{7}Li, ^{23}Na, ^{133}Cs, ^{35}Cl, and ^{81}Br have been measured for alkali halide–poly(ethylene oxide) (PEO)–water mixtures. Addition of PEO to aqueous salt solutions increases the relaxation rates markedly for *all* the nuclei studied. The largest effect has been observed for ^{133}Cs: in a 1.0 *m* CsBr solution containing 45% PEO by weight its relaxation rate is ~65 times larger than that in the polymer-free solution. The increases found are mainly caused by (i) asymmetric hydration of the ions, induced by the PEO, and (ii) direct cation–ether oxygen interactions of the same type—but much weaker—as in metal complexes with crown ethers and similar compounds. From the temperature dependences of the relaxation rates activation energies have been calculated. Addition of PEO raises the activation energy—typically by a factor of ~4 for a PEO-rich sample compared to that of a pure aqueous salt solution—which reflects a stabilization of the water structure, due to the presence of the polymer.

Introduction

Solutions of poly(ethylene oxide) (PEO) have been investigated by NMR spectroscopy for a long time, as can be seen in the literature. Various NMR methods have been used and, accordingly, the spectroscopic results give different pieces of information about the properties of the systems.

Most common are ^{1}H relaxation measurements on the methylene protons of PEO, which have, for instance, been made in different solvents and correlated to the solvent

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