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Compositional Sequence Distribution and Second-Order Markov Statistics in Vinyl Chloride-Vinylidene Chloride Copolymers by Carbon-13 NMR

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Summary

90 MHz-^{1}H-NMR and 22.635 MHz-^{13}C-NMR spectroscopy were used in a study of vinyl chloride-vinylidene chloride copolymers.
Triad sequence distribution of CCl_2 and CHCl carbon was generated for these copolymers and compared to calculated distributions based on Bernoullian, first-order Markov and second-order Markov statistics. It was observed that for samples different in the conditions of preparation including commercial materials in each case different Markov models give the best fit in formally mathematical treatment without kinetic significance but with the aim of interpretation of physical and/or chemical properties of the copolymers.
The 52-56 ppm region of the VC-VDC copolymer spectra is complicated by the superposition of the effects of tacticity, sequence distribution and the presence of both CH and CH_2 carbons.

Introduction

Vinyl chloride-vinylidene chloride (VC-VDC) copolymers were studied previously by Carbon-13 NMR at 22.6 MHz by FIEDLER and KELLER 1976, CARMAN 1980, SCHLOTHAUER 1985 and at 50.3 MHz by KOMOROSKI 1983 (for the spectra see these papers).
Resonance assignments are complicated by the effects of tacticity, sequence distribution, and the presence of both CH and CH_2 carbons with peak overlapping.
Using polymer increment calculations by KELLER and SCHLOTHAUER and the variation of peak intensities in dependence on the composition one can obtain a certain line assignment (here related to HMDS as internal chemical shift standard in accordance with FIEDLER, KELLER, SCHLOTHAUER and KOMOROSKI).
Of course the 50.3 MHz spectra has a better peak resolution and signal to noise ratio than spectra gained at 22.6 MHz. Further improvement in resolution can be obtained by computer resolution enhancement and APT technique as demonstrated successfully by KOMOROSKI and SHOCKCOR. They determined all CCl_2 and CHCl triad sequences quantitatively from the spectra, but they only compared the number-average sequence lengths with calculated values based on Bernoullian and first-order Markov statistics.

Accordingly, this paper describes the application of Bernoullian, first-order and second-order Markov statistics using experimental triad data of different kinds of VC-VDC copolymers including commercial products.
We also used triad concentration results of commercial copolymers (BFGoodrich Co.) given by KOMOROSKI (samples A, B,C). Commercial polymers were obtained from the Buna factories (samples B1, B2). Samples W1 to W3 are identical to those investigated by WANDELT and KRYSZEWSKI.
A significant improvement of the results is achieved by going from Bernoullian to second-order Markov analyses only in the case of the commercial copolymers, while no significant deviations from a first-order Markov model occur for samples prepared to small conversions.

Results and Discussion

The NMR spectra were measured with a Bruker HX 90 R PFT spectrometer.
We assigned the spectra using the variation of peak intensities with composition, the homopolymer spectra and the assignment by the aid of increment methods.
The assignments of the various configurational isomers of VC sequences (AAA, AAB, AA, where A: VC, B: VDC) were given previously by FIEDLER and KELLER (the letters i and s, ii and ss are erroneously changed and should be corrected, compare the assignment of steric n-ads by CARMAN 1973 and INOUE 1972) and SCHLOTHAUER. The configurational assignments only involve sequences of adjacent VC units, because VDC monomer units do not contain an asymmetric center.
In the CCl_2 region, 82..88 ppm, resolution reveals fine structure due to pentad sequences for the ABA and BBA+ABB triads. The peaks at 52..56 ppm are assigned to CHCl carbons with peak overlapping to the CH_2 carbon AB sequence. CH_2 dyads AA (44.5 ppm) and BB (60,8 ppm) are widely separated.
Mole fraction of triads (observed distributions see table) was determined by normalization of the peak areas under the assumption of $P_r = 0.5$, $P_{rr} = P_r^2$, that means a reasonable estimate of AAB+BAA is given by twice the intensity of the well resolved peak A^mAB at 52.4 ppm and of AAA by 4 times A^rA^rA peak intensity at 56.0 ppm.
The composition (mole fractions A, B) for the samples B1, B2, W1-W3, U1-U4 was obtained using ^1H-NMR from the intensities of the methine and the methylene proton part and from the intensities of the methylene proton partial spectra of dyads (well resolved BB centered tetrads) too. The results were in good agreement with those obtained from chemical chlorine analyses. The ^{13}C-NMR composition analysis according to our experience yields results of a little lower precision.

In order to find the best fit of the comonomer arrangements sequence distribution for VC-VDC copolymers, we examine Bernoullian and Markov analysis.
A second-order Markov process requires the specification of eight conditional probabilities, for which we must consider the influence of the relative arrangements of the last three units of the growing chain end (s. BOVEY 1972).

For convenience, we designate these as

$$\begin{array}{lll} P(AA/A) = a & P(AA/B) = \bar{a} & a + \bar{a} = 1 \\ P(AB/A) = b & P(AB/B) = \bar{b} & b + \bar{b} = 1 \\ P(BA/A) = c & P(BA/B) = \bar{c} & c + \bar{c} = 1 \\ P(BB/A) = d & P(BB/B) = \bar{d} & d + \bar{d} = 1 \end{array} \qquad (1)$$

where P(AA/A) is the propability of a A monomer joining a chain end terminating in AA, and so on.
Triad distributions were calculated from

$$\begin{array}{ll} P(AAA) = acds^{-1} & P(ABA) = \bar{a}bds^{-1} \\ \bar{P}(AAB) = 2\bar{a}cds^{-1} & \bar{P}(BBA) = 2\bar{a}\bar{b}ds^{-1} \\ P(BAB) = \bar{a}\bar{c}ds^{-1} & P(BBB) = \bar{a}\bar{b}\bar{d}s^{-1} \end{array} \qquad (2)$$

$$s = \bar{a}\bar{b} + 2\bar{a}d + cd$$

This second-order Markov model reduces to a first-order Markov model when $a = c$ and $b = d$ and to a Bernoullian if $a = b = c = d$, which follows directly from the definitions (1).

We used these relationships for testing the triad distributions, experimentally determined from the peak areas, for conformity to the propagation statistics - see table.
Dyad distributions were also observed quantitatively from the ^{13}C spectra. But for fitting the second-order Markov model at least triad distributions should be available.

It is evident from the table that a significant improvement of the results is acchieved by starting from Bernoullian and going to second-order Markov analysis only for commercial samples B1, B2 and A, B, C (KOMOROSKI), but we didn't find any significant deviations from a first-order Markov model for samples W1-W3, U1-U4.
To illustrate the differences we formally calculated the product of monomer reactivity ratios based on first-order (ROTH et al)

$$r_A r_B^{(1)} = \frac{4(P(AAA) + \bar{P}(AAB)/2)(P(BBB) + \bar{P}(BBA)/2)}{(\bar{P}(AAB) + 2P(BAB))(\bar{P}(BBA) + 2P(ABA))} \qquad (3)$$

and on second-order Markov statistics (ROTH et al using the relations given by CHUJO)

$$r_A r_B^{(2)} = \frac{a\bar{d}}{\bar{a}d} = \frac{4P(AAA)P(BBB)}{\bar{P}(AAB)\bar{P}(BBA)} \qquad (4)$$

for the addition of units A or B to a chain end terminating in AA or BB and

$$r'_A r'_B{}^{(2)} = \frac{c\bar{b}}{\bar{c}b} = \frac{\bar{P}(BAA)\bar{P}(ABB)}{4P(BAB)P(ABA)} \qquad (5)$$

Table: Observed and calculated triad monomer distributions and apparent products of monomer reactivity ratios for VC-VDC copolymers

Micro-structure parameters	Sample B1 P(VC) = 0.399				Sample B2 P(VC) = 0.597			
	Obs.	B.	M.1	M.2	Obs.	B.	M.1	M.2
ABA$^{a)}$	0.086	0.096	0.073	0.084	0.067	0.144	0.056	0.069
BBA+AAB	0.248	0.288	0.264	0.242	0.168	0.194	0.198	0.173
BBB	0.257	0.217	0.240	0.251	0.182	0.065	0.174	0.187
AAA	0.162	0.064	0.113	0.167	0.360	0.213	0.304	0.353
AAB+BAA	0.099	0.191	0.211	0.102	0.130	0.287	0.226	0.128
BAB	0.149	0.144	0.099	0.154	0.093	0.097	0.042	0.091
SD$^{b)}$		0.146	0.135	0.012		0.258	0.127	0.011
$r_A r_B^{(1)}$	1.60				5.49			
$r_A r_B^{(2)}$	2.62				16.07			
$r'_A r'_B{}^{(2)}$	0.92				0.74			
a$^{c)}$		0.399	0.516	0.766		0.597	0.729	0.847
b			0.355	0.410			0.362	0.444
c				0.249				0.411
d				0.325				0.316

Micro-structure parameters	Sample W1 P(VC) = 0.175				Sample W2 P(VC) = 0.327			
	Obs.	B.	M.1	M.2	Obs.	B.	M.1	M.2
ABA	0.025	0.025	0.024	0.024	0.045	0.072	0.044	0.045
BBA+ABB	0.235	0.238	0.229	0.227	0.255	0.296	0.256	0.254
BBB	0.575	0.562	0.554	0.555	0.380	0.305	0.376	0.378
AAA	0.015	0.005	0.016	0.018	0.070	0.035	0.071	0.071
AAB+BAA	0.065	0.051	0.079	0.076	0.160	0.144	0.161	0.162
BAB	0.085	0.119	0.098	0.100	0.090	0.148	0.091	0.091
SD		0.040	0.029	0.029		0.113	0.005	0.003
$r_A r_B^{(1)}$	1.96				2.60			
$r_A r_B^{(2)}$	2.26				2.61			
$r'_A r'_B{}^{(2)}$	1.80				2.52			
a		0.175	0.288	0.316		0.327	0.469	0.467
b			0.171	0.175			0.254	0.261
c				0.277				0.471
d				0.170				0.251

Micro-structure parameters	Sample W3 P(VC) = 0.554				Sample U1 P(VC) = 0.354			
	Obs.	B.	M.1	M.2	Obs.	B.	M.1	M.2
ABA	0.105	0.137	0.105	0.105	0.040	0.081	0.037	0.040
BBA+ABB	0.220	0.220	0.220	0.220	0.220	0.295	0.229	0.221
BBB	0.115	0.089	0.115	0.115	0.360	0.270	0.358	0.362
AAA	0.215	0.170	0.213	0.215	0.135	0.044	0.135	0.134
AAB+BAA	0.260	0.274	0.265	0.260	0.185	0.162	0.181	0.183
BAB	0.085	0.110	0.083	0.085	0.060	0.148	0.061	0.059
SD		0.067	0.006	0		0.179	0.011	0.003
$r_A r_B^{(1)}$	1.60				4.67			
$r_A r_B^{(2)}$	1.73				4.78			
$r'_A r'_B{}^{(2)}$	1.60				4.24			
a		0.554	0.616	0.623		0.354	0.599	0.593
b			0.489	0.488			0.242	0.267
c				0.605				0.607
d				0.489				0.234

Micro-structure parameters	Sample U2 P(VC) = 0.503				Sample U3 P(VC) = 0.608			
	Obs.	B.	M.1	M.2	Obs.	B.	M.1	M.2
ABA	0.060	0.126	0.057	0.059	0.070	0.145	0.071	0.070
BBA+ABB	0.220	0.248	0.220	0.217	0.195	0.187	0.193	0.195
BBB	0.215	0.123	0.211	0.212	0.130	0.060	0.131	0.130
AAA	0.230	0.127	0.232	0.233	0.315	0.225	0.316	0.315
AAB+BAA	0.220	0.251	0.225	0.223	0.245	0.290	0.242	0.245
BAB	0.055	0.124	0.055	0.056	0.045	0.093	0.046	0.045
SD		0.173	0.007	0.006		0.152	0.004	0
$r_A r_B^{(1)}$	3.94				3.55			
$r_A r_B^{(2)}$	4.09				3.43			
$r'_A r'_B{}^{(2)}$	3.67				3.79			
a		0.503	0.673	0.676		0.608	0.723	0.720
b			0.343	0.353			0.424	0.418
c				0.667				0.731
d				0.338				0.429

Micro-structure parameters	Sample U4 $P(VC) = 0.625$ Obs.	B.	M.1	M.2	Sample A (KOMOROSKI) $P(VC) = 0.148$ Obs.	B.	M.1	M.2
ABA	0.075	0.146	0.073	0.074	0.024	0.019	0.016	0.024
BBA+ABB	0.185	0.176	0.185	0.183	0.188	0.215	0.201	0.186
BBB	0.120	0.053	0.118	0.119	0.639	0.618	0.624	0.633
AAA	0.330	0.244	0.336	0.332	0.021	0.003	0.011	0.022
AAB+BAA	0.250	0.293	0.244	0.252	0.036	0.037	0.061	0.038
BAB	0.040	0.088	0.044	0.040	0.091	0.107	0.086	0.097
SD		0.145	0.010	0.004		0.042	0.035	0.009
$r_A r_B^{(1)}$	3.50				1.98			
$r_A r_B^{(2)}$	3.42				7.93			
$r'_A r'_B^{(2)}$	3.85				0.77			
a		0.625	0.734	0.725		0.148	0.264	0.538
b			0.441	0.448			0.139	0.203
c				0.758				0.165
d				0.435				0.128

Micro-structure parameters	Sample B (KOMOROSKI) $P(VC) = 0.688$ Obs.	B.	M.1	M.2	Sample C (KOMOROSKI) $P(VC) = 0.857$ Obs.	B.	M.1	M.2
ABA	0.152	0.148	0.143	0.142	0.096	0.105	0.080	0.082
BBA+ABB	0.133	0.134	0.123	0.124	0.040	0.035	0.037	0.034
BBB	0.027	0.030	0.026	0.025	0.007	0.003	0.004	0.006
AAA	0.370	0.326	0.358	0.380	0.688	0.629	0.691	0.704
AAB+BAA	0.240	0.295	0.291	0.247	0.144	0.210	0.176	0.148
BAB	0.079	0.067	0.059	0.081	0.025	0.018	0.011	0.026
SD		0.072	0.058	0.018		0.089	0.039	0.022
$r_A r_B^{(1)}$	1.14				2.42			
$r_A r_B^{(2)}$	1.25				3.34			
$r'_A r'_B^{(2)}$	0.66				0.60			
a		0.688	0.711	0.755		0.857	0.887	0.905
b			0.700	0.696			0.811	0.828
c				0.603				0.742
d				0.711				0.741

[a] Distribution of triads measured by ^{13}C-NMR (Obs.- observed, B.- Bernoullian, M.1- first-order, M.2- second-order Markov

[b] "Standard Deviations" of the observed and calculated triad distributions (square root of square deviations sum)

[c] Parameters of mathematical fit for different Markov models

for addition A or B to AB, BA.
No differences between $r_A r_B^{(1)}$, $r_A r_B^{(2)}$ and $r'_A r'_B{}^{(2)}$ occur when a first-order Markov model is valid (samples W1-W3, U1-U4). Due to preparation to high conversion it cannot be expected that the commercial products (B1, B2, A, B, C) correspond to simple copolymerization models and $r_A r_B^{(2)}$ and $r'_A r'_B{}^{(2)}$ divergate - see table.
In this sense the formally calculated products of monomer reactivity ratios are without kinetic significance but should serve as features for copolymer sample series manufactured at different conditions.

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