which calculations are based. Relative measures of pore size distributions in different Styragel samples should be obtainable with quite some certainty, however.

Casassa[1] computed the equilibrium constant for the concentration of random coil polymer inside *vs.* outside the pores for a single pore size model using spheres, cylinders, and slabs as the pore shapes. He obtained no correlation with the experimental data of Moore and Arrington[8] for the spherical and cylindrical pore calculations and obtained rather good correlation with the data using the slab model.

No uniqueness is claimed in the present work by the good fit obtained in Figure 3 between the experimental retention time data from Moore and Arrington and the calculated retention times assuming a Gaussian distribution of cylindrical pore sizes and h^2 as the polymer size parameter governing entrapment. In general, if adjustment of a two-parameter model cannot produce calculated results which reasonably match experimental data, the model is obviously incorrect in principle. If a fit is obtained, however, the model may or may not be correct.

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Characterization of Sequence Distribution of Vinylidene Chloride–Vinyl Chloride Copolymers to High Conversions by Nuclear Magnetic Resonance Spectroscopy

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ABSTRACT: Dyad and tetrad sequence concentrations of vinylidene chloride–vinyl chloride copolymers were determined by nmr and successfully compared with those calculated from the copolymerization theory over wide ranges of composition and conversion. The change of the monomer sequence distribution during polymerization is discussed using the relations between the copolymer composition and the sequence concentrations as functions of conversion.

Recently[1,2] we have characterized styrene–methyl methacrylate and vinylidene chloride–vinyl acetate copolymerization systems over the wide ranges of composition and conversion. Both the copolymer composition and the sequence concentration (triad or dyad and tetrad) were determined from nmr measurement and were successfully compared with those expected from the copolymerization theory. Furthermore, we have given the relations between the copolymer composition and the particular sequence concentrations as a function of conversion,[3] by which we could characterize a monomer sequence distribution of a given copolymer sample.

Nmr spectra of vinylidene chloride–vinyl chloride copolymers were recently analyzed by the dyad and tetrad assignments by Johnsen[4] and Enomoto and Satoh.[5] Since this system is technically important, it is useful to examine the nmr spectra up to high conversions and to compare the results with other copolymerization systems in the light of the monomer sequence distribution.

Experimental Section

Copolymer samples were prepared by suspension polymerization at 50° using azobisisobutyronitrile as a catalyst. Nmr spectra were measured at 80–90° in thionyl chloride using a Japan Electron Optics C-60 spectrometer working at 60 Mc/sec.

Results and Discussion

Figure 1 shows the typical CH_2 proton nmr spectra of copolymers prepared from a monomer feed of 30 mol % vinylidene chloride to 13, 38, and 92% conversions. The dyad and tetrad assignments as indicated in the figure, where A and B represent vinylidene chloride and vinyl chloride units, respectively, have been established in the literatures.[4,5] The resonances at higher magnetic fields increase in peak strengths with conversion, indicating the increasing incorporation of the less reactive vinyl chloride monomer as polymerization proceeds. Therefore, by measuring the corresponding peak areas of the normal CH_2 proton spectra, we can readily estimate the dyad concentrations $\overline{P_2\{AA\}}$, $\overline{P_2\{AB\}}$ or

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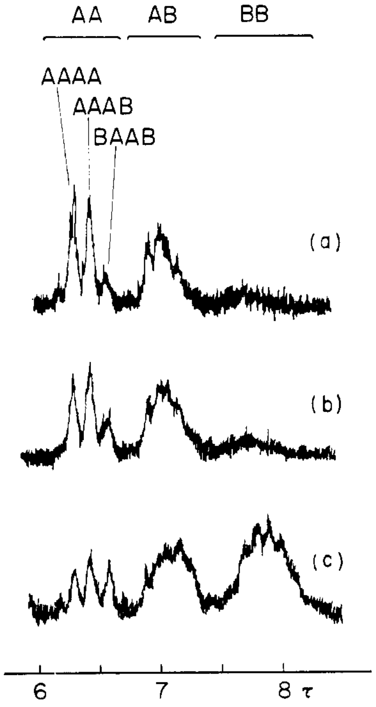

Figure 1. CH_2 proton nmr spectra of vinylidene chloride–vinyl chloride copolymers prepared from a monomer feed of $f_A{}^\circ = 0.30$. Mole-fractional conversions, *m*: (a) 0.13, (b) 0.38, (v) 0.92.

$\overline{P_2\{BA\}}$, and $\overline{P_2\{BB\}}$, and the tetrad concentrations $\overline{P_4\{AAAA\}}$, $\overline{P_4\{AAAB\}}$ or $\overline{P_4\{BAAA\}}$, and $\overline{P_4\{BAAB\}}$, all in units of mole fractions. Normalization under the stationary condition requires that

$$\overline{P_2\{AA\}} + 2\overline{P_2\{AB\}} + \overline{P_2\{BB\}} = 1 \qquad (1)$$

$$\overline{P_2\{AA\}} = \overline{P_4\{AAAA\}} + 2\overline{P_4\{AAAB\}} + \overline{P_4\{BAAB\}} \qquad (2)$$

where $\overline{P_2\{AB\}} = \overline{P_2\{BA\}}$ and $\overline{P_4\{AAAB\}} = \overline{P_4\{BAAA\}}$. The mole fractions of all vinylidene chloride and vinyl chloride units, denoted by $\overline{P_1\{A\}}$ and $\overline{P_1\{B\}}$, respectively, can also be estimated by eq 3–5.

$$\overline{P_1\{A\}} + \overline{P_1\{B\}} = 1 \qquad (3)$$

$$\overline{P_1\{A\}} = \overline{P_2\{AA\}} + \overline{P_2\{AB\}} \qquad (4)$$

$$\overline{P_1\{B\}} = \overline{P_2\{BB\}} + \overline{P_2\{AB\}} \qquad (5)$$

The upper horizontal lines in the notations, $\overline{P_n\{\cdots\}}$, were drawn in order to distinguish the quantities for the actual copolymers, which are the averages over the observed conversions, from those for the instantaneous copolymers, $P_n\{\cdots\}$. Therefore $\overline{P_n\{\cdots\}}$ is related to $P_n\{\cdots\}$ by the relation

$$\overline{P_n\{\cdots\}} = \frac{1}{m}\int_0^m P_n\{\cdots\}\,dm \qquad (6)$$

where *m* is the mole-fractional conversion.

Theoretical sequence concentrations according to the usual copolymerization theory were calculated by the following procedure. First, the instantaneous monomer composition, f_A or f_B, was calculated as a function of mole-fractional conversion using the integrated form of the Skeist equation.[6–9] Second, the instantaneous copolymer composition and sequence concentrations were calculated by probability relations[10]

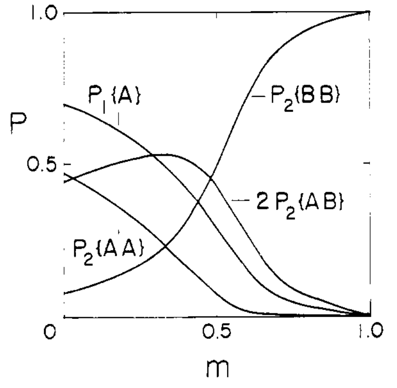

Figure 2. Instantaneous copolymer composition and dyad concentrations as a function of mole-fractional conversion, $f_A{}^\circ = 0.30$.

$$P_1\{A\} = P_{BA}/(P_{BA} + P_{AB}) = 1 - P_1\{B\} \qquad (7)$$

$$P_2\{AA\} = P_1\{A\}P_{AA} \qquad (8)$$

$$P_2\{AB\} = P_2\{BA\} = P_1\{A\}P_{AB} = P_1\{B\}P_{BA} \qquad (9)$$

$$P_2\{BB\} = P_1\{B\}P_{BB} \qquad (10)$$

$$P_4\{AAAA\} = P_1\{A\}P_{AA}{}^3 \qquad (11)$$

$$P_4\{AAAB\} = P_4\{BAAA\} = P_1\{A\}P_{AA}{}^2 P_{AB} = P_1\{B\}P_{BA}P_{AA}{}^2 \qquad (12)$$

$$P_4\{BAAB\} = P_1\{B\}P_{BA}P_{AA}P_{AB} = P_1\{A\}P_{AA}P_{AB}{}^2 \qquad (13)$$

where P_{AB}, for example, is the conditional probability of an A unit being followed by a B unit in the copolymerization propagation sequence, so that

$$P_{AB} = 1 - P_{AA} = 1/(1 + r_A x) \qquad (14)$$

$$P_{BA} = 1 - P_{BB} = 1/(1 + r_B/x) \qquad (15)$$

where

$$x = f_A/f_B \qquad (16)$$

The quantities r_A and r_B are the respective monomer reactivity ratios, which were obtained from the nmr data on low-conversion copolymers in the usual manner as $r_A = 4.5 \pm 0.5$, and $r_B = 0.16 \pm 0.03$ in fair accord with the reported values.[11] Finally, the integrated copolymer composition and sequence concentration of the copolymers, which had been formed during the mole-fractional conversions, *m*, were obtained by numerically integrating the corresponding instantaneous relations by eq 6.

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TABLE I

EXPERIMENTAL AND THEORETICAL COPOLYMER COMPOSITION, DYAD AND TETRAD CONCENTRATIONS

Feed	Mole-fractional	$\overline{P_1\{A\}}$		$\overline{P_2\{AA\}}$		$\overline{2P_2\{AB\}}$		$\overline{P_2\{BB\}}$		$\overline{P_4\{AAAA\}}$		$\overline{2P_4\{AAAB\}}$		$\overline{P_4\{BAAB\}}$	
$f_A{}^0$	conversion	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
0.72	0.09	0.92	0.95	0.85	0.89	0.14	0.11	0.01	0.00	0.73	0.68	0.12	0.16	0.02	0.06
0.72	0.46	0.90	0.93	0.82	0.86	0.18	0.14	0.01	0.00	0.66	0.66	0.14	0.15	0.02	0.05
0.72	0.79	0.85	0.89	0.72	0.78	0.25	0.22	0.03	0.00	0.54	0.55	0.17	0.19	0.03	0.04
0.49	0.10	0.82	0.82	0.67	0.67	0.30	0.31	0.03	0.03	0.44	0.42	0.20	0.19	0.02	0.06
0.49	0.38	0.78	0.79	0.60	0.62	0.35	0.35	0.04	0.04	0.36	0.33	0.21	0.22	0.03	0.06
0.49	0.91	0.54	0.61	0.36	0.42	0.36	0.38	0.27	0.20	0.19	0.23	0.14	0.15	0.04	0.04
0.30	0.13	0.67	0.69	0.43	0.46	0.47	0.46	0.11	0.08	0.18	0.21	0.20	0.20	0.05	0.06
0.30	0.38	0.59	0.61	0.34	0.38	0.50	0.48	0.16	0.15	0.12	0.13	0.16	0.15	0.06	0.09
0.30	0.92	0.34	0.32	0.16	0.15	0.34	0.34	0.50	0.51	0.05	0.04	0.08	0.07	0.04	0.05
0.14	0.09	0.44	0.45	0.18	0.21	0.52	0.48	0.30	0.31	0.03	0.05	0.09	0.09	0.06	0.07
0.14	0.43	0.30	0.27	0.09	0.08	0.40	0.39	0.50	0.53	0.01	0.02	0.04	0.03	0.04	0.03
0.14	0.87	0.17	0.17	0.05	0.07	0.24	0.20	0.70	0.74	0.01	0.02	0.02	0.01	0.02	0.03

Typical results of the calculations are shown in Figures 2–4, starting from the initial monomer composition of 30 mol % vinylidene chloride. The instantaneous relations given in Figure 2 show that the more reactive monomer, vinylidene chloride, is rapidly consumed before about 70% conversion. $P_1\{A\}$ and $P_2\{AA\}$ decrease and $P_2\{BB\}$ increases sharply, while $P_2\{AB\}$ constitutes a small plateau during this initial 70% conversion, after which essentially only vinyl chloride monomers remain in the mixture to produce very long sequences of vinyl chloride. Similar but smoother trends are apparent in the integrated relations in Figure 3. The nmr data indicated by circles show good fit to the theoretical lines up to 92 mol % conversion investigated. For the tetrad concentrations in Figure 4, however, the agreement is not as good, particularly for $\overline{P_4\{BAAB\}}$, because the experimental error is quite large due to the very small peak areas of these resonances.

Table I gives the experimental and theoretical copolymer compositions and dyad and tetrad concentrations of several copolymer samples of different compositions and conversions. This table again shows good agreement between experiment and theory except for sequences having very small concentrations. Therefore we conclude that in the present system also, the nmr analyses are quite compatible with the usual copolymerization theory over the whole range of composition and conversion. Consequently, it will be useful for practical purposes to provide a theoretical diagram for characterizing monomer sequence distribution as a function conversion, as will be shown below.

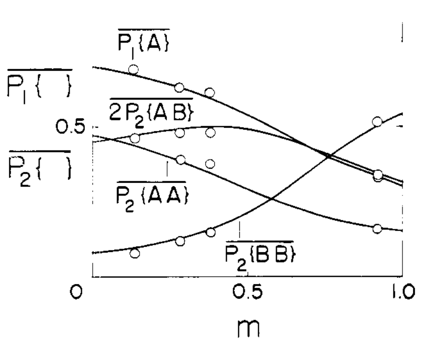

Figure 3. Integrated copolymer composition and dyad concentrations as a function of mole-fractional conversion, $f_A{}^\circ = 0.30$.

Figures 5 and 6 show the theoretical relations between the integrated copolymer composition and the dyad or tetrad concentrations for the 0, 80, and 100 mol % conversions. The lines for which $m = 0$, corresponding to the relations for random monomer sequence distribu-

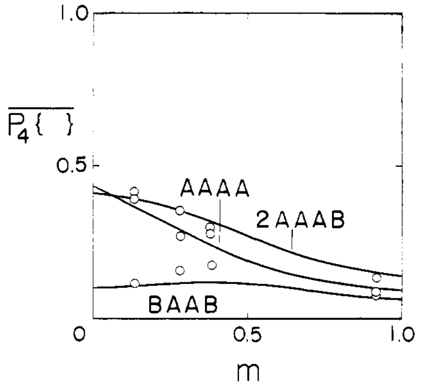

Figure 4. Integrated tetrad concentrations as a function of mole-fractional conversion, $f_A{}^\circ = 0.30$.

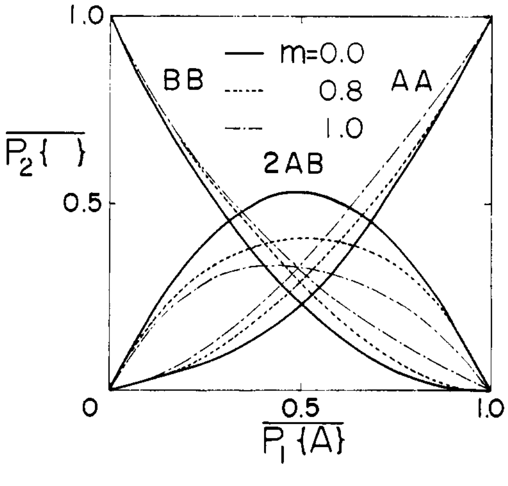

Figure 5. Integrated dyad concentrations *vs.* copolymer composition.

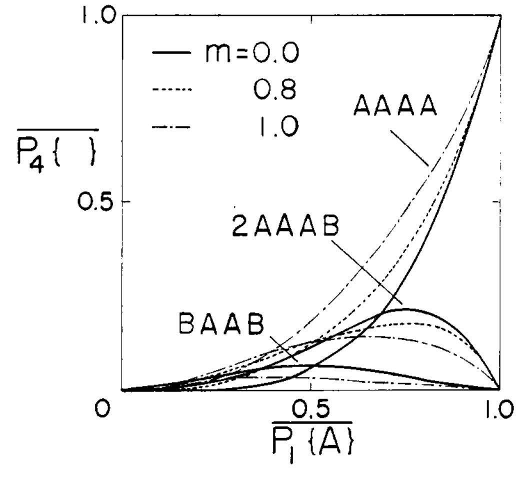

Figure 6. Integrated tetrad concentrations *vs.* copolymer composition.

tion, do not change much up to a mole conversion of about 60%. However, as polymerization proceeds beyond about 80%, the sequence distribution becomes quite broad, as reflected by the increased $\overline{P_2\{\mathrm{AA}\}}$ and $\overline{P_2\{\mathrm{BB}\}}$ and by the decreased $\overline{P_2\{\mathrm{AB}\}}$, resulting from the formation of long vinyl chloride sequences in the later stage of polymerization. The apparent sequence lengths (number average) calculated by eq 17 and 18

$$l_{\mathrm{A}} = \overline{P_1\{\mathrm{A}\}/P_2\{\mathrm{AB}\}} \qquad (17)$$

$$l_{\mathrm{B}} = \overline{P_1\{\mathrm{B}\}/P_2\{\mathrm{AB}\}} \qquad (18)$$

show this trend more clearly, as given in Figure 7.

As compared with the present system, the previously reported vinylidene chloride-vinyl acetate system,[3] where the monomer reactivity ratios are 6.7 and 0.05, respectively, shows a more, pronounced change of the monomer sequence distribution with conversion. Already at 50% conversion, the latter system shows con-

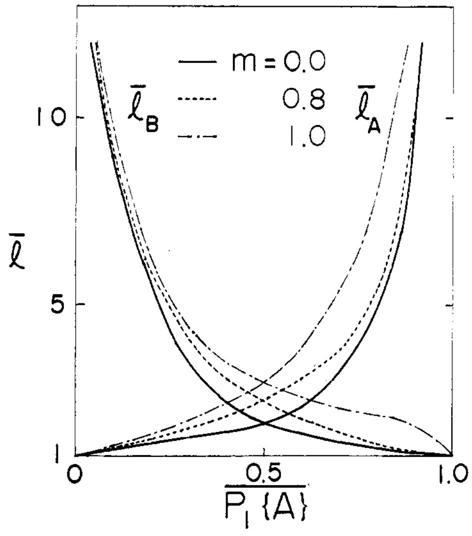

Figure 7. Apparent sequence lengths *vs.* copolymer composition.

siderable deviations from the random sequence distributions, similar to those found for 80% conversion in the former system. Thus the reactivity difference between the pertinent monomer pairs is most decisive for the change of monomer sequence distribution during polymerization, as expected. The styrene-methyl methacrylate system[2,3] (monomer reactivity ratios, 0.45 and 0.50) shows no change in the relations between the copolymer composition and the triad sequence distributions with conversions from 0 to 100%.

Since we can readily estimate all the quantities in the ordinates and abscissas of Figures 5–7 from nmr data, we can use these figures for characterizing a given copolymer sample in the light of the monomer sequence distribution and therefore also for checking a copolymerization process (such as conversion or feed composition) from nmr measurements.