as compared to their phantom counterparts. This is implied by the fact that the topological environment of the un-cross-linked polymer is carried over to the cross-linked counterpart.

Although in form the preceding theory appears to be similar to the theory of Langley,[14] it is in fact quite different. The latter theory has been discussed at length by Queslel and Mark.[15] In the Langley theory, one has no way of separating the effect of topological constraints from the phantom network, because the strain dependence of the constraint network is unspecified. Therefore, the conclusions one would draw from the Langley theory are dependent on the assumption made about the relation of the chemical composition of the network to the modulus due to chemical cross-links. In our theory, no such assumption is necessary, because we obtain both moduli from experimental data.

We would like to point out that the conclusions we have drawn are not expected to be valid near the gel point. We have also based all of our conclusions on data on randomly cross-linked, tetrafunctional networks. Major differences are not expected for end-linked networks. The value of ξ would probably depend on network functionality. Most of the available data on networks that are not tetrafunctional are on PDMS. Unfortunately, PDMS has a very low G_N^0 so that the values of G_N would be relatively small. This fact precludes a study of the functionality dependence of ξ.

Registry No. PEA (homopolymer), 9003-32-1.

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Stereochemical Kinetics of Anionic Vinyl Polymerization. 2. ^{13}C NMR Analysis of Poly(2-vinylpyridine) and Poly(4-vinylpyridine) Terminated with Labeled End Groups

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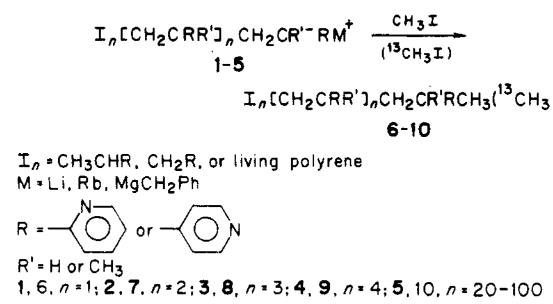
ABSTRACT: Carbon-13 NMR spectra of the ^{13}C-labeled methyl end group of poly(2-vinylpyridine) (P-2-VP), poly(4-vinylpyridine) (P-4-VP), and poly(2-isopropenylpyridine) (P-2-IP) were stereochemically assigned on the basis of known model compounds. It was found that in the case of P-2-VP the chain-end stereochemistry differed appreciably from that of the chain itself. For P-4-VP and P-2-IP, these stereochemistries are nearly identical. These results are shown to reveal consistency with a Bernoullian process for P-4-VP and P-2-IP and consistency with a second- or higher-order Markoff process in the case of P-2-VP. The results suggest that stereochemical comparison of end group and chain may be a valuable new method for analyzing the statistics of vinyl polymers prepared by anionic polymerization.

Introduction

We have recently reported the trapping of lithium salts of stereoisomeric "living" poly(2-vinylpyridine) anions by reaction with ^{13}C-labeled CH_3I followed by ^{13}C NMR analysis of the labeled end group[1] (eq 1). It was shown that the stereoisomeric composition fo the dyad flanking the carbanion differed from that of the chain itself as determined by ^{13}C NMR of the quaternary pyridine carbon. Such a pattern was previously shown to be consistent with the occurrence of a Markoff-type process in which the stereoisomeric composition of the chain end affects its rate of tactic monomer addition.[2-4] Such a process is not inconceivable for the anionic polymerization of 2-vinylpyridine in media of low polarity and in the presence of small counterions. Thus, in the case of Li or Na ion in THF, a strong coordination of the counterion with the nitrogen lone pair of the penultimate 2-pyridine ring has been demonstrated for both short-chain and longer chain living poly(2-vinylpyridine).[5,6] Inspection of CPK models shows that, in the case of tetramers and longer chains, the chelation tends to position the third asymmetric center in close proximity to the carbanion. As a result, a Markoff-type process is not implausible. The detection of Markoffian statistics in vinyl polymers from determination



$$I_n^-M^+ + (n+1)CH_2{=\!=}CRR' \longrightarrow$$

$$\underset{\mathbf{1-5}}{I_n[CH_2CRR']_nCH_2CR'^-RM^+} \xrightarrow[(^{13}CH_3I)]{CH_3I} \underset{\mathbf{6-10}}{I_n[CH_2CRR']_nCH_2CR'RCH_3(^{13}CH_3)} \quad (1)$$

I_n = CH_3CHR, CH_2R, or living polyrene
M = Li, Rb, $MgCH_2Ph$
R = or
R' = H or CH_3
1, 6, n = 1; **2**, **7**, n = 2; **3**, **8**, n = 3; **4**, **9**, n = 4; **5**, 10, n = 20–100

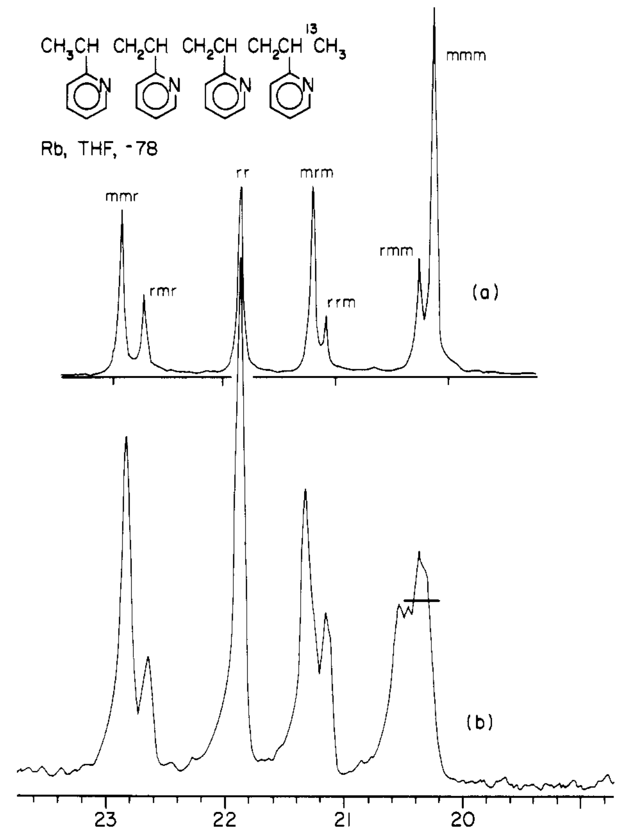


Figure 1. 75-MHz ^{13}C NMR spectra of 2-VP tetramer and polymer (in o-dichlorobenzene-d_4) prepared in THF at -78 °C in the presence of Rb ion.

of the frequency of the various multiads is far from simple, since tetrad and pentad information is required to rule out first- and second-order Markoff processes, respectively.[7] Such detailed information, even from ^{13}C NMR, is rarely available in vinyl polymers because of line broadening caused by a variety of factors. More seriously, the stereochemical assignment of the various *n*-ads frequently makes it necessary to choose a statistical process by which these *n*-ads are related, thus making suspect the verification of a particular mechanism. As a result, the verification of the statistics of vinyl polymerization by an independent method is of considerable interest.

Experimental Section

The alkali[6] and magnesium[14] salts of 2-ethyl- or 2-methylpyridine were prepared as previously described. Lithio-2-ethylpyridine was recrystallized from hexane/THF (90/10 v/v). Lithium tetraphenylboride was prepared by cation exchange of $NaBPh_4$ and LiCl in THF at 25 °C and was recrystallized in 1,2-dichloroethane followed by drying in vacuo.[20] The polymerizations were carried out by in vacuo distillation of monomer onto the rapidly stirred initiator solution over a period of 1–2 h, followed by distillation of ^{13}C-enriched (50%) CH_3I.[6] Poly(2-vinylpyridine) was precipitated from THF solutions by addition of *n*-hexane followed by drying in vacuo. Poly(4-vinylpyridine) and poly(2-isopropenylpyridine) were recovered in a similar manner by precipitation in aqueous solutions of methanol from toluene solutions.

NMR spectra were obtained in CD_3OD solutions (15% w/v) at 25 °C or in o-dichlorobenzene/C_6D_5Br solutions (15% w/v) at 130 °C at 300 MHz (^{1}H) or 75 MHz (^{13}C).

Results

Anionic polymerization of 2- or 4-vinylpyridine (2- or 4-VP) or 2-isopropenylpyridine (2-IP)[8,9] was carried out by initiation in THF, toluene, or benzene using alkali salts of 2-ethylpyridine, magnesium salts of 2-methylpyridine, or living polystyryllithium as initiator. Figure 1, a and b, shows the spectra of the labeled methyl group of the symmetrical 2-VP tetramer 8 (I = CH_3CHR where R = 2-pyridyl, n = 3) and the corresponding polymer prepared in the presence of Rb ion in THF at -78 °C. Four groups of absorptions corresponding to the mm, rm, rr, and mr terminal triads are observed with additional fine splitting, corresponding to the presence of a prior m or r dyad, in each absorption except rr.[1,6]

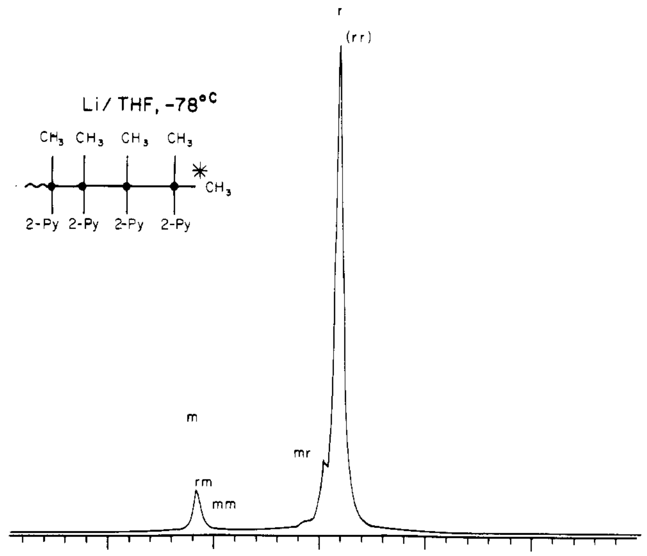


Figure 2. 75-MHz ^{13}C NMR spectrum in o-$C_6H_4Cl_2$/C_6D_5Br at 130 °C of poly(2-isopropenylpyridine) prepared in THF at -78 °C in the presence of Li ion and terminated with ^{13}C-labeled CH_3I.

The spectrum of the labeled methyl group of poly(4-vinylpyridine) is very similar to that of poly(2-vinylpyridine).[10] The spectrum of poly(2-isopropenylpyridine)[8] prepared in the presence of Li ion in THF at -78 °C and terminated with $^{13}CH_3I$ is shown in Figure 2. The corresponding stereochemical assignments in each of these cases (Table I) are based on stereochemically well-defined model compounds and are unambiguous.[6,9–11] The stereochemistry of poly(2- or 4-vinylpyridine) and that of poly(2-isopropenylpyridine) are based upon the ^{13}C NMR spectra of the quaternary ring carbon and the ^{1}H NMR spectra of the α-methyl group, respectively.[8,12,13]

The effects of certain reaction variables such as the mode of monomer addition (vapor phase or one-time addition of liquid monomer), the presence of common ion in the case of Li ion in THF, and the concentration of initiator were investigated. Furthermore, the effects of solvent (THF or aromatic hydrocarbon) and of counterion were also determined. The results are shown in Tables I and II.

The polymerization of 2-VP in THF in the presence of Li or Rb ion is moderately isotactic-like. The effects of carbanion concentration, the mode of monomer addition, and the mode of addition of methyl iodide (during or after monomer addition) do not appear to greatly influence the stereochemistry of the chain or the chain end in the case where Li is the counterion. Only the addition of lithium tetraphenylboride appears to measurably increase the isotactic content of the chain and the chain end. In toluene, the poly(2-VP) prepared with Li initiators depends strongly on the amount of residual THF present in the initiator, the isotactic triad content increasing to ~70% for the polymerization initiated in toluene by polystyryllithium prepared in the absence of THF. For the polymerization initiated with benzylpicolylmagnesium[14] in THF,

Table I
Chain-End and Main-Chain Stereochemistry of Poly(2-VP), Poly(4-VP), and Poly(2-IP) as a Function of Polymerization Conditions[a]

				chain			chain end			
run no.	M$^+$/solvent	monomer	T, °C	f_{mm}	f_{mr}	f_{rr}	f_{mm^-}	f_{mr^-}	f_{rm^-}	f_{rr^-}
1	Li/THF[b]	2-VP	−78	0.44	0.47	0.09	0.30	0.33	0.21	0.16
2	Li/THF[c]	2-VP	−78	0.44	0.40	0.16	0.31	0.26	0.26	0.17
3	Li/THF[d]	2-VP	−78	0.52	0.35	0.13	0.40	0.33	0.13	0.14
4	Li/THF[e]	2-VP	−78	0.42	0.40	0.18	0.29	0.28	0.25	0.18
5	Li/THF[f]	2-VP	−78	0.51	0.39	0.10	0.42	0.36	0.12	0.12
6	Li/THF[g]	2-VP	−78	0.56	0.36	0.08	0.42	0.34	0.12	0.12
7	Li/Tol[h]	2-VP	−78	0.46	0.39	0.14	0.34	0.26	0.25	0.15
8	Li/Tol[i]	2-VP	−78	0.56	0.31	0.13	0.41	0.28	0.17	0.14
9	Li/Tol[j]	2-VP	−78	0.69	0.21	0.10	0.39	0.29	0.19	0.13
10	Li/THF	4-VP	−78	0.26	0.51	0.23	0.27	0.23	0.27	0.23
11	Li/THF	2-IP	−78	0.01	0.12	0.87	0.01	0.10	0.07	0.82
12	Rb/THF[k]	2-VP	−78	0.50	0.36	0.14	0.37	0.34	0.15	0.14
13	Mg/THF[l]	2-VP	25	0.37	0.56	0.07	0.29	0.30	0.26	0.15
14	Mg/Tol[l]	2-VP	25	0.76	0.18	0.06	0.53	0.19	0.20	0.07
15	Mg/C_6H_5[l]	2-VP	25	0.92	0.07	0.01	0.50	0.17	0.25	0.08

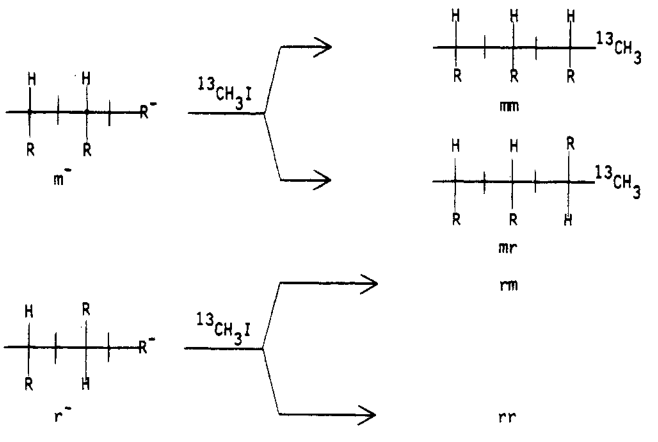
[a] Carbanion concentration ≅ 5×10^{-3} M. [b] Concentration = 2.0×10^{-2} M. [c] Single addition of liquid monomer. [d] [$LiBPh_4$]/[initiator](I) = 0.30. [e] Methylation occurred during monomer addition. [f] [$LiBPh_4$]/[I] = 0.40. [g] [$LiBPh_4$]/[I] = 2.0. [h] Two equivalents of THF present in initiator. [i] Initiated with oligostyryllithium in toluene (~9×10^{-3} M). [j] Initiated with oligostyryllithium (~3×10^{-3} M). [k] Initiated by rubidio-2-ethylpyridine. [l] Initiated by benzylpicolylmagnesium, one-time addition of liquid monomer.

Table II
Comparison of Stereochemical Parameters of the Chain and the Chain End of Poly(2-VP), Poly(4-VP), and Poly(2-IP) Calculated for a First-Order Markoff Process

		chain				chain end	
run no.	ion/solvent/monomer	P_{mr}[a]	P_{rm}[a]	ρ[b]	f_m/f_{m^-}[c]	$P_{mr}*$[d]	$P_{rm}*$[d]
1	Li/THF/2-VP	0.35	0.72	0.93	1.32	0.41	0.67
2	Li/THF/2-VP	0.31	0.56	1.20	1.15	0.46	0.60
3	Li/THF/2-VP	0.25	0.57	1.20	1.21	0.25	0.70
4	Li/THF/2-VP	0.32	0.53	1.20	1.18	0.47	0.60
5	Li/THF/2-VP	0.27	0.66	1.06	1.30	0.24	0.78
6	Li/THF/2-VP	0.25	0.69	1.07	1.37	0.23	0.74
7	Li/Tol/2-VP	0.30	0.21	1.15	1.16	0.42	0.63
8	Li/Tol/2-VP	0.22	0.54	1.34	1.21	0.29	0.67
9	Li/Tol/2-VP	0.13	0.51	1.55	1.37	0.33	0.69
10	Li/THF/4-VP	0.50	0.50	0.98	0.95	0.50	0.52
11	Li/THF/2-IP	0.86	0.07	1.08	1.01[e]	0.88	0.11
12	Rb/THF/2-VP	0.26	0.56	1.21	1.31	0.29	0.71
13	Mg/THF/2-VP	0.43	0.80	0.81	1.18	0.47	0.67
14	Mg/Tol/2-VP	0.11	0.60	1.42	1.16	0.26	0.73
15	Mg/C_6H_6/2-VP	0.04	0.78	1.23	1.27	0.33	0.68

[a] Calculated from $P_{mr} = f_{mr}/(2f_{mm} + f_{mr})$ and $P_{rm} = f_{mr}/(2f_{rr} + f_{mr})$. [b] Calculated from chain triads as $f_m f_r/f_{mr}$. [c] f_m is calculated from the chain triads as $f_{mm} + f_{mr}/2$; f_{m^-} is calculated from chain-end triads as $f_{mm} + f_{mr}$. [d] Calculated from eq 6. [e] Calculated as f_r/f_{r^-}.

Scheme I



poly(2-VP) appears to be more heterotactic-like. In toluene or benzene, this polymerization leads to highly isotactic polymers as reported by others.[15] For the polymerization of 4-VP in THF in the presence of Li ion, the stereochemistry is clearly atactic, but for 2-IP under these conditions, the polymer is highly syndiotactic, as previously reported.[8]

Scheme I shows that the proportions of propagating carbanions flanked by meso and racemic dyads, m$^-$ and r$^-$, respectively, are given by

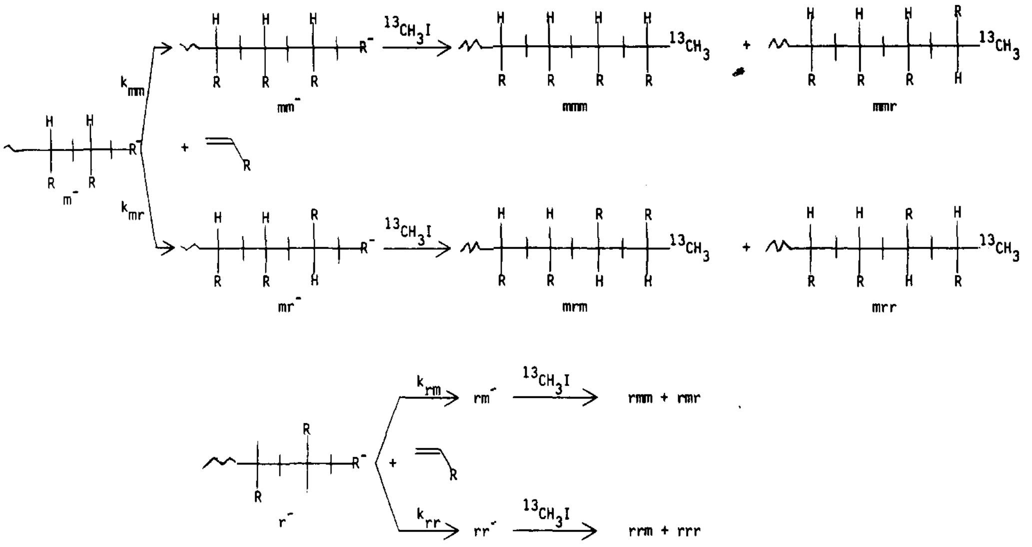
$$f_{m^-} = f_{mm} + f_{mr} \qquad f_{r^-} = f_{rr} + f_{rm} \tag{2}$$

It is clear that the stereochemistry of methylation reflected in the last dyad of the chain does not affect the fractions of m$^-$ and r$^-$ anions. Furthermore, if the stereochemical composition of the last three dyads is known, the proportions of mm$^-$, rm$^-$, mr$^-$, and rr$^-$ chain ends may be determined. Interestingly, the meso content (f_m) of poly(2-VP), as determined from triad tacticity, is seen to differ considerably from f_{m^-}, the f_m/f_{m^-} ratio varying from 1.1 to 1.4 (Tables I and II). The corresponding ratio for the other two polymers, however, is quite close to 1. Thus, the stereoisomeric compositions of the chain and the chain end appear to differ for poly(2-VP), whereas they appear to be virtually identical for poly(4-VP) and poly(2-IP).

Discussion

Elias and co-workers[2,3] have shown that differences in

Scheme II



the stereochemistry of the chain end and the chain of vinyl polymers are consistent with the occurrence of Markoff processes (Scheme II). Following steady-state conditions, we have for chains of sufficient degree of polymerization

$$d[m^-]/dt = k_{rm}[r^-][M] - k_{mr}[m^-][M] = 0$$

so that

$$f_{m^-} = [m^-]/([m^-] + [r^-]) = k_{rm}/(k_{rm} + k_{mr})$$

$$f_{r^-} = k_{mr}/(k_{rm} + k_{mr}) \qquad (3)$$

where $[m^-]$, f_{m^-}, $[r^-]$, and f_{r^-} denote the concentrations and fractions of meso or racemic chain ends, respectively. The meso content, f_m, of the chain itself is given by[2,3]

$$f_m = k_{rm}/(k_{rm} + k_{mr}k_r/k_m) \qquad (4)$$

where $k_r = k_{rr} + k_{rm}$ and $k_m = k_{mm} + k_{mr}$ denote the rate constants of propagation for r^- and m^- anions, respectively. From eq 3 and 4, it is clear that the inequality $f_m \neq f_{m^-}$ should, in general, hold for a first-order Markoff process unless $k_r = k_m$. For a Bernoullian Chain, this should generally be the case, so that in this case the stereochemical compositions of chain end and chain are expected to be identical. Therefore, the inequality $f_m \neq f_{m^-}$ should be a valuable additional criterion to distinguish between Bernoullian and Markoff processes. Thus, on the basis of the above data, the anionic polymerizations of 2-VP appear to be non-Bernoullian and consistent with first-order Markoff statistics. However, the stereochemical end-group information contained in the spectra provides information on the stereochemistry of the second dyads adjoining the carbanion center. Thus, the fractions of the corresponding stereoisomeric carbanions are determined from

$$\begin{aligned} f_{mm^-} &= f_{mmm} + f_{mmr}; \qquad & f_{mr^-} &= f_{mrm} + f_{mrr}; \\ f_{rm^-} &= f_{rmm} + f_{rmr}; \qquad & f_{rr^-} &= f_{rrm} + f_{rrr} \end{aligned} \qquad (5)$$

Following steady-state conditions, we can write

$$\begin{aligned} d[mr^-]/dt &= k_{mr}[m^-][M] - k_r[mr^-][M] = 0 \\ d[rm^-]/dt &= k_{rm}[r^-][M] - k_m[rm^-][M] = 0 \end{aligned} \qquad (6)$$

Substituting eq 3 into eq 6 leads to

$$[rm^-] = \frac{k_{rm}[r^-]}{k_m} \quad \text{or} \quad f_{rm^-} = \frac{k_{rm}k_{mr}}{k_m(k_{mr} + k_{rm})} \qquad (7a)$$

where

$$f_{rm^-} = [rm^-]/([r^-] + [m^-])$$

Similarly

$$f_{mr^-} = k_{rm}k_{mr}/(k_r[k_{mr} + k_{rm}]) \qquad (7b)$$

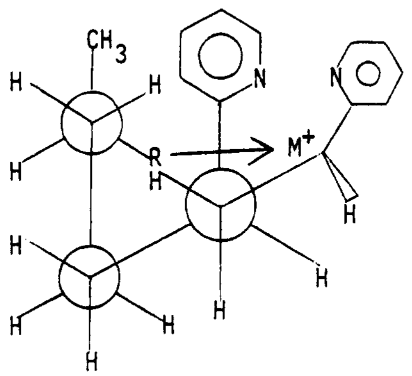
and using eq 3 leads to

$$f_{rm^-} = \frac{k_{mr}}{k_m}f_{m^-} = P_{mr}{}^*f_{m^-} \qquad f_{mr^-} = \frac{k_{rm}}{k_r}f_{r^-} = P_{rm}{}^*f_{r^-}$$

where $k_{mr}/k_m = P_{mr}{}^*$ and $k_{rm}/k_r = P_{rm}{}^*$ denote the conditional first-order Markoff probabilities. As a result, these parameters may be determined from the analysis of the end groups and compared with the two first-order Markoff parameters, P_{rm} and P_{mr}, obtained from triad analysis:

$$P_{mr} = \frac{f_{mr}}{2f_{mm} + f_{mr}}; \qquad P_{rm} = \frac{f_{mr}}{2f_{rr} + f_{mr}}$$

For a first-order Markoff process, the parameters obtained from the chain and the chain end will be equal. The inequalities $P_{mr} \neq P_{mr}{}^*$ and $P_{rm} \neq P_{rm}{}^*$ should therefore signify noncompliance with a first-order Markoff process. The occurrence of such a process may be checked, therefore, without having to resort to tetrad analysis. From Table II, the ratio f_m/f_{m^-} for poly(2-VP) exceeds 1 by a considerable margin, in most cases indicating non-Bernoullian statistics. Of particular interest is the fact that even in cases where the persistence ratio ρ is close to 1, the f_m/f_{m^-} ratio considerably exceeds 1 (runs 1, 5, 6). In terms of a first-order Markoff process, $k_r < k_m$. However, the inequalities $P_{mr} \neq P_{mr}{}^*$ and $P_{rm} \neq P_{rm}{}^*$ also hold in almost all cases, and this suggests that a first-order Markoff process does not seem to describe the data (Table II). These results, particularly those in THF, are of interest. In this case, in the presence of Li ion, the polymerization has been shown to proceed through an intermediate in which the counterion is chelated by the penultimate pyridine ring.[5] Inspection of CPK models shows that in such a case, the carbanion may be brought into close proximity to the third asymmetric center from the carbanion as schematically shown for tetramer anion **3**. Such a structure may lead one to propose second-order Markoff statistics. However, for the 2-VP polymerization in the presence of Rb ion where complexation should be virtually



[3]

nonexistent, the process does not appear to be Bernoullian (f_m/f_{m^-}) = 1.31) nor first-order Markoff ($P_{rm}^* \neq P_{rm}$, $P_{mr} \neq P_{mr}^*$).

Although the anionic polymerization of 2-VP in THF is believed to proceed through ion pairs, the participation of other ionic species such as free ions or triple ions should be considered. Thus, even if each of two such possible polymerization sites propagates according to a Bernoullian mechanism, the overall Coleman–Fox statistics may be expected to be non-Bernoullian or even non-Markoffian.[16] However, neither increasing the initiator concentration nor the presence of lithium tetraphenylboride in Li-initiated polymerizations in THF significantly affected the non-Bernoullian, non-first-order Markoffian character of the polymerization.

It should be pointed out that for the polymerization of 2-VP, the f_m/f_{m^-} ratio always exceeds 1, but that the persistence ratio, ρ, varies from 0.81 (Mg/THF) to 1.2 (Li/THF). In view of the fact that the mechanism of polymerization of 2-VP in the presence of small counterions is not yet fully clear, the relationship between ρ and f_m/f_{m^-} remains to be elucidated.

Recent NMR studies of model 2-VP dimer and trimer anions have shown that the propagating anions exist as a mixture of *E* and *Z* geometric isomers.[17] These studies have also shown these carbanion isomers do not interconvert on the polymerization time scale but should be interconverted upon addition of monomer, depending on the transition-state monomer conformation. It may be shown that such a two-site model is expected to lead to non-Bernoullian and non-Markoffian chains.[18] Whether the above data are due to such a process or are caused by a second- or higher-order Markoff process remains to be seen.

In contrast to the results obtained for 2-VP, the two polymerizations carried out with 4-VP and 2-IP in THF appear to be clearly consistent with Bernoullian statistics using all three criteria (ρ, f_m/f_{m^-}, and P and P^* values). This is not unreasonable, since the stereochemistry of anionic polymerization of 2-IP in THF has been suggested to be mainly determined by steric interactions.[8] The anionic polymerization of 4-VP in THF also is expected to be radically different from that of 2-VP.[10,19] In this case, intramolecular chelation of the type indicated for 2-VP is essentially impossible, and the *E* and *Z* isomers do not occur.

In conclusion, these studies indicate for the first time that the comparison of chain and chain-end stereochemistry may be of considerable value in elucidating the statistics of vinyl polymerization without the need for tetrad or pentad analysis. Further studies along these lines are in progress.

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Registry No. Poly(2-VP) (homopolymer), 25014-15-7; poly(4-VP) (homopolymer), 25232-41-1; poly(2-IP) (homopolymer), 37824-36-5.

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