NOTES

Estimation of Sequence Distribution in Poly(vinyl acetate)

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We found a good method to saponify poly(vinyl ester)s with bulky ester groups and determined their tacticities by ^1H NMR spectrum of resulted poly(vinyl alcohol) (PVA).¹ The tacticities of poly(vinyl ester)s were found to vary with bulkiness of ester groups² and cotacticities of copolymers of vinyl acetate (VAc) with vinyl propionate (VPr),³ vinyl decanoate (VD)⁴ and vinyl pivalate (VP)⁵ varied with feed monomer composition. Although cotacticities were not well simulated by the terminal model for copolymers of VAc with VP indicating some penultimate effects, they were well simulated for copolymers of VAc with VPr and VD by the terminal model.⁶ Hence, we consider that homo-polymerizations of VAc, VPr, and VD can be explained by the terminal model and sequences in these polymers can be estimated by random numbers (Sequence distribution in copolymer of styrene with α -methyl styrene, etc. were simulated by Monte Carlo method⁷). The present paper reports estimation of the sequence distribution in poly(vinyl acetate) (PVAc) using random numbers with drand 48 in the UNIX system. The sequences can be estimated by Bernoulli's

statistics, but we consider that the Monte Carlo method has some merits. For example, sequence distributions estimated can be drawn as shown in Figure 1 and the estimation can be carried out for P_n as shown in Table I.

In the case of PVAc with $P_n = 1000$, random numbers of 1–1000 were generated by a computer. The polymerization of VAc obeys the terminal model and the isotactic parameter (σ) is 0.474. Thus random numbers of 1–474 were assigned to meso diad, and those of 475–1000 to racemo diad. Sequence distributions were determined and an example is shown in Figure 1.

As shown in the figure, long sequences as r_{11} and m_8 could be observed. The frequencies of r and m were counted, and the ratios of r/m , rr/mm and $rrrr/mmmm$ were calculated. The procedures were repeated $10^7/P_n$ times and the ratios were averaged. The values for 5 examples and the average values are listed in Table I.

Sequence distributions for other P_n were also determined in the same manner, and the ratios were calculated as shown in Table I. The ratios determined by Bernoulli's statistics are listed in Table I.

Figure 1. Example of sequence distribution in poly(VAc) obtained by radical polymerization at 0°C. $P_n = 1000$; $\sigma = 0.474$; $r/m = 1.06$; $rr/mm = 1.28$; $rrrr/mmmm = 1.59$.

Good reproducibility in the ratios and good agreement of ratios obtained by Monte Carlo and Bernoulli's were found for high P_n (> 1000), but reproducibility of the ratios, especially $rrrr/mmmm$, was not good for low P_n (≤ 1000). These results suggest that sequence distributions in each PVAc molecule with small P_n are quite different. However, the average values of $rrrr/mmmm$ for PVAc with respective P_n , except $P_n = 100$, are not so much different from each other. Values of r/m and rr/mm were in good agreement with those determined by ^1H NMR spectrum. Values of $rrrr/mmmm$ were

a little different from those determined by the ^{13}C NMR spectrum (we consider that the difference may be caused by penultimate effect). The sequence distributions generated by computer are considered to represent approximately those in actual PVAc.

We consider that such long racemo sequences as r_{11} are important factors for the properties of PVA such as gelation of PVA aq solution. We are investigating the sequence distributions of the other poly(vinyl ester)s and the results will be reported in the near future.

Table I. Estimated ratios of *racemo* and *meso* sequences in PVAc obtained by radical polymerization at 0°C

Run	P_n	r/m	rr/mm	$rrrr/mmmm$
A1	100	0.852	0.727	0.385
A2		0.887	0.762	0.400
A3		1.50	2.12	15.0
A4		0.961	0.923	0.750
A5		1.33	2.00	∞
—	—	—	—	—
Average ^a		1.13(0.232)	1.36(0.608)	
B1	500	1.06	1.11	1.06
B2		0.916	0.843	0.882
B3		1.08	1.06	1.35
B4		1.03	1.06	0.939
B5		1.11	1.25	1.70
—	—	—	—	—
Average ^a		1.11(0.101)	1.25(0.230)	1.70(0.877)
C1	1000	1.07	1.13	1.59
C2		1.21	1.46	2.74
C3		1.03	1.07	1.43
C4		1.04	1.08	1.04
C5		1.03	1.06	1.17
—	—	—	—	—
Average ^a		1.11(0.070)	1.24(0.158)	1.60(0.512)
D1	5000	1.09	1.18	1.63
D2		1.15	1.34	1.74
D3		1.07	1.14	1.15
D4		1.08	1.16	1.29
D5		1.10	1.21	1.50
—	—	—	—	—
Average ^a		1.11(0.032)	1.23(0.071)	1.53(0.211)
E1	10000	1.12	1.25	1.53
E2		1.09	1.20	1.35
E3		1.10	1.22	1.29
E4		1.10	1.22	1.54
E5		1.15	1.33	1.83
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Table I. (continued.)

Run	P_n	r/m	rr/mm	$rrrr/mmmm$
Average		1.11(0.023)	1.23(0.051)	1.52(0.149)
Found	7870	1.11 ^b	1.23 ^b	1.75(0.0082) ^c
Calculated ^d		1.11	1.23	1.52

^a From $10^7/P_n$ times (one cycle of drand 48) calculation. Values in () are standard deviations.

^b Measured by ^1H NMR spectrum of PVA derived from PVAc.

^c Measured by ^{13}C NMR spectrum of PVA derived from PVAc. Value in () is standard deviation.

^d Calculated by Bernoulli's statistics.

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