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Antepenultimate Copolymer Composition Equation

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SUMMARY

A new reduced copolymer composition equation weighing the effects of units through the antepenultimate is derived for the first time. The simplification obtained is placed into context with previously published work.

This paper reports the derivation of a simplified binary copolymer composition equation including contributions from all antepenultimate units. Derivations of antepenultimate copolymer equations have been previously reported with certain simplifying assumptions [1] or with excessive complexity [2-4].

The crux of the problem is the derivation of expressions for P_{aab}, P_{baa}, P_{bba}, and P_{abb}, weighing antepenultimate unit contributions, for substitution in the equations [1] which weigh penultimate unit contributions.

$$P_{ab} = \frac{P_{aab}}{P_{aab} + P_{baa}} \tag{1}$$

$$P_{ba} = \frac{P_{bba}}{P_{bba} + P_{abb}} \tag{2}$$

Suitable expressions for P_{aab} and P_{bba} were offered but P_{baa} and P_{abb} may have been oversimplified [1]. Ito and Yamashita [3] offered overly complex expressions for P_{baa} and P_{abb}, but correctly pointed out that they could not be derived in the simple way possible for P_{aab} and P_{bba}. In their derivation Ito and Yamashita made use of their Eqs. (2.6) and (2.7).

$$P_3\{BAA\} = P_4\{ABAA\} + P_4\{BBAA\} \tag{3}$$

$$P_3\{ABB\} = P_4\{AABB\} + P_4\{BABB\} \tag{4}$$

It has now been found possible to derive expressions for P_{baa} and P_{abb} by invoking the principle of sequence reversibility [1]. Thus

$$P\{BBABA\} = P\{ABABB\} \tag{5}$$

Such sequence probabilities may be expressed in terms of the probability of finding an initial sequence multiplied by conditional probabilities.

$$P\{BBA\}\, P_{bbab}P_{bbaba} = P\{AB\}P_{aba}P_{abab}P_{ababb} \tag{6}$$

Assuming

$$P\{BBA\} = P\{ABB\} \tag{7}$$

one may write

$$P\{AB\}P_{abb}P_{bbab}P_{bbaba} = P\{AB\}P_{aba}P_{abab}P_{ababb} \tag{8}$$

Since expressions including only antepenultimate unit effects are sought, it follows that

$$P_{bbaba} = P_{baba} \tag{9}$$

and

$$P_{ababb} = P_{babb} \tag{10}$$

We obtain

$$P_{abb}P_{bbab}P_{baba} = P_{aba}P_{abab}P_{babb} \tag{11}$$

Since

$$P_{aba} = 1 - P_{abb} \tag{12}$$

$$\frac{P_{abb}}{1 - P_{abb}} = \frac{P_{abab}P_{babb}}{P_{bbab}P_{baba}} \tag{13}$$

$$P_{abb} = \frac{P_{abab}P_{babb}}{P_{bbab}P_{baba} + P_{abab}P_{babb}} \tag{14}$$

Similarly, starting with

$$P\{AABAB\} = P\{BABAA\} \tag{15}$$

$$P\{AAB\}P_{aaba}P_{aabab} = P\{BA\}P_{bab}P_{baba}P_{babaa} \tag{16}$$

Since

$$P\{AAB\} = P\{BAA\} \tag{17}$$

we may write

$$P\{BA\}P_{baa}P_{aaba}P_{aabab} = P\{BA\}P_{bab}P_{baba}P_{babaa} \tag{18}$$

$$P_{baa}P_{aaba}P_{abab} = P_{bab}P_{baba}P_{abaa} \tag{19}$$

It follows that

$$P_{baa} = \frac{P_{baba}P_{abaa}}{P_{aaba}P_{abab} + P_{baba}P_{abaa}} \tag{20}$$

Substituting P_{abb} and P_{baa} from Eqs. (14) and (20), respectively, and

$$P_{aab} = \frac{P_{aaab}}{P_{aaab} + P_{baaa}} \tag{21}$$

$$P_{bba} = \frac{P_{bbba}}{P_{bbba} + P_{abbb}} \tag{22}$$

from Refs. 1 and 3 into Eqs. (1) and (2) we obtain

$$P_{ab} = 1 + \frac{1 + \dfrac{P_{abbb}}{P_{bbba}}}{1 + \dfrac{P_{aaba}P_{abab}}{P_{baba}P_{abaa}}} \tag{23}$$

$$P_{ba} = 1 + \frac{1 + \dfrac{P_{baaa}}{P_{aaab}}}{1 + \dfrac{P_{bbab}P_{baba}}{P_{abab}P_{babb}}} \tag{24}$$

Since

$$\frac{P\{A\}}{P\{B\}} = \frac{P_{ba}}{P_{ab}} \tag{25}$$

we obtain on substitution

$$\frac{P\{A\}}{P\{B\}} = \frac{1 + \dfrac{1 + \dfrac{P_{baaa}}{P_{aaab}}}{1 + \dfrac{P_{bbab}P_{baba}}{P_{abab}P_{babb}}}}{1 + \dfrac{1 + \dfrac{P_{abbb}}{P_{bbba}}}{1 + \dfrac{P_{aaba}P_{abab}}{P_{baba}P_{abaa}}}} \tag{26}$$

Expressed in terms of reacting monomer concentrations and monomer reactivity ratios [1] we obtain an interesting simplification

$$\frac{P\{A\}}{P\{B\}} = \frac{1 + \dfrac{1 + \dfrac{r_1'x(r_1x + 1)}{r_1'x + 1}}{1 + \dfrac{x(r_1''x + 1)}{r_2''(r_1'''x + 1}}}{1 + \dfrac{1 + \dfrac{r_2'(r_2/x + 1)}{x(r_2'/x + 1)}}{1 + \dfrac{r_2''/x + 1}{r_1''x(r_2'''/x + 1)}}} \tag{27a}$$

CONVENTIONS

$P_{aaab} = 1/(r_1 x + 1)$	$r_1 = k_{aaaa}/k_{aaab}$
$P_{baaa} = r_1'x/(r_1'x + 1)$	$r_1' = k_{baaa}/k_{baab}$
$P_{bbab} = 1/(r_1'''x + 1)$	$r_1'' = k_{abaa}/k_{abab}$
$P_{baba} = 1/(r_2''/x + 1)$	$r_1''' = k_{bbaa}/k_{bbab}$
$P_{abab} = 1/(r_1''x + 1)$	$r_2 = k_{bbbb}/k_{bbba}$
$P_{abbb} = (r_2'/x)/(r_2'/x + 1)$	$r_2' = k_{abbb}/k_{abba}$
$P_{bbba} = 1/(r_2/x + 1)$	$r_2'' = k_{babb}/k_{baba}$
$P_{aaba} = 1/(r_2'''/x + 1)$	$r_2''' = k_{aabb}/k_{aaba}$
	$x = A/B$ (unreacted monomers)

It only remains to estimate the degree of over-simplification involved in the use [1] of

$$P_{baa} = \frac{1}{1 + \dfrac{P_{abab}}{P_{bbaa}}} \tag{27}$$

for example, in lieu of

$$P_{baa} = \frac{1}{1 + \dfrac{P_{aaba}P_{abab}}{P_{baba}P_{abaa}}} \tag{14}$$

and similarly for P_{abb}. It may be shown that the difference is no greater than the limitation to a penultimate unit effect in two of the four governing probabilities, P_{baa} and P_{abb}. Equations (27) and (14) reduce to the same equation in these circumstances

$$P_{baa} = \frac{1}{1 + \dfrac{P_{bab}}{P_{baa}}} \tag{28}$$

Actually, the difference is probably much less than indicated above. It may be shown by equating the right sides of Eqs. (27) and (14) and simplifying as shown

$$\frac{1}{1 + \dfrac{P_{abab}}{P_{bbaa}}} = \frac{1}{1 + \dfrac{P_{aaba}P_{abab}}{P_{baba}P_{abaa}}} \tag{29}$$

$$P_{baba}P_{abaa}(P_{bbaa} + P_{abab}) = (P_{baba}P_{abaa} + P_{aaba}P_{abab})P_{bbaa} \tag{30}$$

$$P_{baba}P_{abaa} = P_{aaba}P_{bbaa} \tag{31}$$

that the only condition necessary is for this proportionality to hold

$$\frac{P_{baba}}{P_{aaba}} = \frac{P_{bbaa}}{P_{abaa}} \tag{32}$$

Thus, B in the antepenultimate position must have the same effect relative to A whether followed by AB or BA.

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