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Publisher *Taylor & Francis*

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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

On Terpolymerization Theory

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To cite this Article Sawada, Hideo(1967) 'On Terpolymerization Theory', Journal of Macromolecular Science, Part A, 1: 3, 559 – 560

To link to this Article: DOI: 10.1080/10601326708053989

URL: <http://dx.doi.org/10.1080/10601326708053989>

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LETTER TO THE EDITOR

On Terpolymerization Theory

For systems of three monomers Ham (1) has proposed that the relation

$$P_{ab}P_{bc}P_{ca} = P_{ac}P_{cb}P_{ba} \quad (1)$$

should hold but no theoretical proof was given. Here P_{ab} is the probability of monomer B adding to a chain ending in monomer A in the presence of monomers, A, B, and C, and so on.

In the present note we wish to derive Eq. (1) from the assumption that any special interactions between A· and B and between B· and A (and so on) are symmetrical. From this assumption, we have

$$N_{ab} = N_{ba} \quad (2)$$

$$N_{bc} = N_{cb} \quad (3)$$

$$N_{ca} = N_{ac} \quad (4)$$

where N_{ab} and N_{ba} refer to the percentages of linkages of AB and BA in the copolymer, and so on.

The percentage of AB linkages in the copolymer is given by

$$N_{ab} = aP_{ab} \quad (5)$$

Similarly,

$$N_{ba} = bP_{ba} \quad (6)$$

where a and b refer to the molar percentages of monomer units in the copolymer. We have, therefore,

$$aP_{ab} = bP_{ba} \quad (7)$$

Similarly, two other equations can be derived:

$$bP_{bc} = cP_{cb} \quad (8)$$

$$cP_{ca} = aP_{ac} \quad (9)$$

Then the product of left sides of Eqs. (7) to (9) is

$$(aP_{ab})(bP_{bc})(cP_{ca}) \quad (10)$$

The product of right sides of Eqs. (7) to (9) is

$$(bP_{ba})(cP_{cb})(aP_{ac}) \quad (11)$$

As Eq. (10) is equivalent to Eq. (11), it can be shown that

$$(aP_{ab})(bP_{bc})(cP_{ca}) = (bP_{ba})(cP_{cb})(aP_{ac}) \quad (12)$$

Dividing both sides by (abc) yields

$$P_{ab}P_{bc}P_{ca} = P_{ac}P_{cb}P_{ba} \quad (1)$$

If steady-state concentrations of chain ends can be assumed for systems of three monomers, it can be proved that

$$N_{ab} + N_{ac} = N_{ba} + N_{ca} \quad (13)$$

$$N_{ba} + N_{bc} = N_{ab} + N_{cb} \quad (14)$$

If $N_{ab} = N_{ba}$, the following relations are shown, from Eqs. (13) and (14):

$$N_{bc} = N_{cb} \quad (3)$$

$$N_{ac} = N_{ca} \quad (4)$$

Therefore, Eq. (1) can be true only when $N_{ab} = N_{ba}$.

Acknowledgment

The author wishes to thank Daicel Limited for permission to publish this work.

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*Received by editor August 29, 1966
Submitted for publication November 14, 1966*