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Asymmetry of Monomer Unit Arrangements in Multicomponent Polymers

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Asymmetry of Monomer Unit Arrangements in Multicomponent Polymers

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SUMMARY

The concept of "flux" is proposed for quantitatively describing the manner in which the relative concentrations of three chain ends remain at a steady state in a terpolymerization. The flux is a measure of the net rate of transition from one chain end to another. If a terpolymerization remains at a steady state with respect to the relative concentrations of the three chain ends, then the flux must be either zero or some finite number which is independent of the choice of chain ends used to calculate it. It is a necessary and sufficient condition for Ham's concept of sequence reversibility to be true that the flux be zero. The flux calculated for many systems using reactivity ratio data is quite near zero. However, the calculations necessarily share the imprecision of reactivity ratio data. Terpolymer sequence distribution data, if available, could be used in a proposed method of calculating flux.

Stimulated by Ham's postulate of "sequence reversibility" which led to simplified equations for composition in multicomponent polymerizations [1], a number of papers have appeared [2-6] which either dispute or support the concept put forward by Ham. The purpose of the present note is to place this concept in a better perspective and to propose a means for testing it experimentally.

In the case of a binary copolymer of monomers A and B, the inherent symmetry of a copolymer chain demands that the probability of finding an AB sequence in the finished chain is identical to that of finding a BA sequence. This statement depends only on the chain being of a high degree of polymerization; it does not depend on the manner of chain formation. It was as an extrapolation of this fact that Ham postulated that, in a terpolymer of monomers A, B, and C, the probability of finding some sequence, say ABCA, might be just the same as finding its reverse, ACBA. This is expressed by

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

where P_{ij} is the conditional probability that a chain ending in monomer i will add monomer j.

$$P_{ij} = k_{ij}[M_j] / \sum_{j=A,B,C} k_{ij}[M_j] \qquad (2)$$

Let us denote a terpolymerization of monomers A, B, and C by the following

$$\begin{tikzcd} & a \arrow[dl, shift left] \arrow[dr, shift left] & \\ b \arrow[ur, shift left] \arrow[rr, shift left] & & c \arrow[ul, shift left] \arrow[ll, shift left] \end{tikzcd} \qquad (3)$$

where a, b, and c represent chains ending in monomers A, B, and C, respectively, and the arrows denote the addition of the monomer required to convert one chain end to another. Not shown in such a representation is the addition of a given monomer unit to its own chain end. If we regard the terpolymerization as being at a steady state, the relative concentrations of a, b, and c must remain unchanged. This can be so either if each transition is individually balanced,

$$a \rightleftharpoons b;\ b \rightleftharpoons c;\ c \rightleftharpoons a \qquad (4)$$

or if there is a net balance around the cycle,

$$\begin{tikzcd} & a \arrow[dr] & \\ b \arrow[ur] & & c \arrow[ll] \end{tikzcd} \qquad (5)$$

In Eq. (4) each step is individually balanced so that, for example, the net number of changes from a to b is the same as from b to a. In Eq. (5), by contrast, each step is not individually balanced, but the net number of changes from a to b is the same as from b to c and the same as from c to a. Equation (4) is superficially similar to the microbalancing of a triangular reaction at equilibrium and will be realized when Ham's postulate (Eq. 1) obtains.

Ham and others have clearly demonstrated that in many cases the use of his postulate is consistent with available data. Unfortunately, reactivity ratio data are not sufficiently precise to provide an unequivocal test of the truth of Ham's postulate. A priori, there is no reason to believe that all systems follow either Eq. (4) or Eq. (5).

To put the problem in a quantitative perspective, let us define the net rate of a transition from chain end i to chain end j as

$$R_{ij} = k_{ij}[i][M_j] - k_{ji}[j][M_i] \qquad (i \neq j) \qquad (6)$$

In the steady state we must have

$$R_{ab} = R_{bc} = R_{ca} \qquad (7)$$

The total rate of polymerization is

$$R = \sum_{i,j} k_{ij}[i][M_j] \qquad (8)$$

where the summation is for i, j taking all values possible including i = j.

We now define the flux for transition from chain end i to chain end j as

$$FL_{ij} \equiv 300R_{ij}/R = 300(F_iP_{ij} - F_jP_{ji}) \qquad (9)$$

where F_i is the mole fraction of monomer i in the terpolymer chain being produced at steady state.

When the microbalancing postulate as represented by Eq. (1) and (4) holds, then the value of the flux will be zero. When Eq. (5) obtains, then the absolute value of the flux will be between zero and 100. A value of 100 would be found if additions only take place in one direction around the cycle and no homo-additions are allowed. In general, one would not expect to find values approaching 100.

If the flux is positive in the abc direction around the cycle, there are more AB diads than BA along the chain in the direction of propagation, more BC than CB, more CA than AC, and more ABC than ACB. Clearly such a polymer does not have symmetry (as does a binary copolymer or a terpolymer formed with zero flux), and it can be said that this polymer has a direction.

In Table 1 we tabulate the flux calculated for a number of terpolymerization systems using available reactivity ratios. The flux has values from about zero to 6 on the arbitrary scale of zero to 100. If one calculates the H value introduced by Mayo [2],

$$H \equiv r_{ab}r_{bc}r_{ca}/r_{ac}r_{cb}r_{ba} \tag{10}$$

there is no quantitative correlation with the flux. There is, however, a qualitative correlation in that negative flux values are obtained when $H < 1.0$ and positive when $H > 1.0$. For $H = 1.0$, one expects the flux to be zero.

The precision of the flux values in Table 1 can be no better than that of the reactivity ratios used to calculate them. As pointed out by Tidwell and Mortimer in their recent review [7], reactivity ratio data are usually too imprecise to permit their use in making fine distinctions, such as that of calculating flux to be zero or nonzero. Therefore Table 1 cannot distinguish between the situation of Eqs. (4) and (5). The asymmetry of the polymer chain could be determined directly by measuring sequence distributions. There are six diad relations (only five are independent) of the form

$$F_{aa} = F_aP_{aa} \text{ and } F_{ab} = F_aP_{ab} + F_bP_{ba} \tag{11}$$

where F_{aa} is the mole fraction of AA diads. There are also three independent restraints of the form

$$P_{aa} + P_{ab} + P_{ac} = 1 \tag{12}$$

Using the eight independent equations of the form of Eqs. (11) and (12), it is not possible to determine the nine unknown conditional probabilities P_{ij}

Table 1. Flux[a]

Monomers[b]			Data used[c]							
1	2	3	r_{12}	r_{13}	r_{21}	r_{23}	r_{31}	r_{32}	Flux	H
MMA	AN	VDCL	1.2	2.53	0.15	0.91	0.24	0.37	-4.88	1.87
ST	MMA	AN	0.51	0.41	0.48	1.2	0.040	0.15	1.97	0.83
ST	α-MST	NMA	1.18	0.48	0.36	0.14	0.46	0.50	1.45	0.88
ST	MAH	MMA	0.042	0.48	0.00	0.03	0.46	3.5	-1.35	—
ST	AN	AA	0.41	0.25	0.040	0.13	0.45	6.0	5.79	0.40
MMA	MA	VA	2.3	20.0	0.47	9.0	0.015	0.10	1.72	0.33
ST	MA	VCL	0.75	35.0	0.18	9.0	0.067	0.083	0.15	0.86
MMA	MA	VCL	2.3	15.0	0.47	9.0	0.02	0.083	0.69	0.71
AN	MA	VCL	0.43	3.7	0.95	9.0	0.074	0.083	0.08	0.98
VCL	VA	AN	1.8	0.074	0.60	0.07	3.7	6.0	-1.12	1.75
VCL	VA	MA	1.8	0.083	0.60	0.03	0.9	5.8	3.13	0.17
VA	VB	NVP	0.35	0.205	0.99	0.44	3.3	2.45	- .19	1.02
VCL	VA	VCB	1.8	5.2	0.60	4.0	0.09	0.15	-1.80	1.38

[a] Flux was calculated at $[M_A] = [M_B] = [M_c] = 1/3$

[b] MMA = methyl methacrylate, AN = acrylonitrile, VDCL = vinylidene chloride, ST = styrene, α-MST = α-methylstyrene, AA = acrylic acid, MA = methyl acrylate, VA = vinyl acetate, VCL = vinyl chloride, VB = vinyl benzoate, NVP = N-vinylpyrolidone, VCB = vinylene carbonate, MAH = maleic anhydride.

[c] From *Copolymerization*, G. Ham, ed., Wiley (Interscience), New York, 1964.

from diad measurements alone. However, if for example the following triad measurement is known,

$$F_{bab} = F_b P_{ba} P_{ab} \tag{13}$$

then the transition probabilities and the flux may be calculated. Determination of sequence distributions in terpolymers is an experiment which can be envisioned [8, 9], but as yet no experimental determinations have been reported. Rabinovitch has recently discussed sequence distributions in terpolymers but reported no experimental data [10].

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