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Derivation of the Quantity of Catenanes in Equilibrium Polymeric Mixtures

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Synopsis. A theoretical consideration is introduced regarding catenation in an equilibrium mixture. The quantity of catenane from rings i and j is expressed as $[\phi(i, j)] \simeq \Phi PE\, [Ri][Rj]$. The symbols Φ, P, and E denote the catenation probability, the overlapping probability and the penetration probability. At θ points or above a critical monomer concentration C^*, $E \simeq 1$. Then, the above equation leads to the analogous form reported previously.[1]

Some theoretical considerations have been reported concerning catenation from two cyclic substances.[1,5] However, there has not been any report that theoretically preestimated the catenane distribution in an equilibrium system; this should be practically important for a characterization of such extensively established industrial materials as polyester, Nylon and polyoxymethylene, or should be one of the guiding principles for challenging a non-bonding polymer gel, one of the most attractive materials that have never been realized. This paper is presented with the aim of preestimating the yields of catenanes in equilibrium, the fundamental idea of which is based on cyclization[2] and entanglement theorems.[3]

Theory

Consider a polymer solution with the Flory distribution D in a volume V and mark half of the randomly chosen molecules red. Then, each will have the equal distribution D and the following equilibria will be established.

A: red.

$$C_{i+x} \rightleftarrows C_i + C_x$$
$$C_i \rightleftarrows R_i$$

B: white.

$$C_{j+y} \rightleftarrows C_j + C_y$$
$$C_j \rightleftarrows R_j$$

Here, C denotes a linear chain, subscripts i, j, x, and y the arbitrary numbers of repeating units and R a cyclic molecule. Then, some ratio of R_i and R_j will encounter and entangle to form a catenane $\phi(i, j)$. Thus, the above equilibria can be rewritten as the following equilibria:

$$C_{i+x} \overset{K_1}{\rightleftarrows} C_i + C_x, \tag{1}$$

$$C_{j+y} \overset{K_2}{\rightleftarrows} C_j + C_y, \tag{2}$$

$$C_i \overset{K_3}{\rightleftarrows} R_i, \tag{3}$$

$$C_j + R_i \overset{K_4}{\rightleftarrows} (C_jR_i), \tag{4}$$

$$(C_jR_i) \overset{K_5}{\rightleftarrows} \phi(i,j), \tag{5}$$

Eqs. 1—5 reduce to

$$C_{i+x} + C_{j+y} \overset{K}{\rightleftarrows} C_x + C_y + \phi(i,j), \tag{6}$$

Equation 1 represents the process in which fragment C_x is released from a permitted angle $\delta\omega$ in a small volume v_s constrained around the terminal atom of fragment C_i to the whole volume V of the system. Assuming that the probabilities of lying in v_s and $\delta\omega$ are independent,† the entropy change of K_1 can be written[2]

$$e^{\Delta S/R} = \left(\frac{1}{\sigma_C}\right)(4\pi V/\delta\omega v_s N_A), \tag{7}$$

where σ_C is the number of the reaction sites of the chain if those have an equal chemical reactivity.

Let ΔH_1 be the enthalpy change of K_1. Then, the equilibrium constant of Eq. 1 is written

$$K_1 = \left(\frac{1}{\sigma_C}\right)(4\pi V/\delta\omega v_s N_A)e^{-\Delta H_1/RT}. \tag{8}$$

Similarly, we have

$$K_2 = \left(\frac{1}{\sigma_C}\right)(4\pi V/\delta\omega v_s N_A)e^{-\Delta H_2/RT}. \tag{9}$$

Equation 3 represents the process that one end of C_i is confined within the angle $\delta\omega$ in volume v_s around another terminal atom to form a new chemical bond. Let σ_{R_i} be the number of the reaction sites of the ring and $W(0)$ the probability that the end-to-end distance is zero. Then, as already pointed out, the equilibrium constant is expressed as

$$K_3 = \left(\frac{\sigma_C}{\sigma_{R_i}}\right)(\delta\omega/4\pi)W_i(0)v_s e^{-\Delta H_3/RT}. \tag{10}$$

Equation 4 represents the process in which C_j and R_i overlap one another under the condition of the phantom molecules. Let this probability be $P(i, j)$. $P(i, j)$ is given

$$P(i,j) = \frac{4\pi S^3 N_A}{3V}, \tag{11}$$

where S is the radius of the overlapping volume.

Now, let $E(i, j)$ be the probability for one molecule

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† This is a reasonable assumption since the chain must be sufficiently long (30 bonds or more) for the catenation to occur.[1]

to move into the sphere of another molecule. Then, E should be equal to the ratio of the probability lying inside the sphere to that lying outside the same. If we define ψ as the volume fraction of segments per unit volume, the probaility that all of a given sequence of x lattice sites are available for occupancy by another chain molecule is $(1-\psi)^x$. Then, E is

$$E(i,j)=\left(\frac{1-\psi_i}{1-\psi_o}\right)^x, \tag{12}$$

where subscripts i and o denote the inside of the molecule and the outside, respectively. Note that ψ is not the real volume, but the excluded volume of the segment.[4] Hence, we may let

$$\begin{aligned} K_4 &= P(i,j)\cdot E(i,j) \\ &= (4\pi S^3N_A/3V\cdot[(1-\psi_i)/(1-\psi_o)]^x. \end{aligned} \tag{13}$$

Equation 5 represents the process in which the one end of C_j meets the another end, accompanying the interlocking with R_i. If the probability for the interlocking, Φ, is independent of the cyclization probability, applying the expression in K_3 we have

$$K_5 = \Phi\cdot(\sigma_C/\sigma_{R_j})\cdot(\delta\omega/4\pi)\cdot W_j\cdot(\mathbf{0})\cdot v_s\cdot e^{-\Delta H_5/RT} \tag{14}$$

The product of K_1—K_5 gives the equilibrium constant of Eq. 6:

$$\begin{aligned} K = \prod_k K_k &= \Phi\cdot[V^2\cdot P\cdot E/\sigma_{R_i}\cdot\sigma_{R_j}\cdot N_A^2]\cdot \\ & W_i(\mathbf{0})\cdot W_j(\mathbf{0})\cdot \mathrm{e}^{-\Delta H/RT}, \end{aligned} \tag{15}$$

where $\Delta H = \sum_k \Delta H_k$.

Also, the following relationship is established in the solution:

$$K = \frac{[C_x]\cdot[C_y]\cdot[\phi(i,j)]}{[C_{i+x}]\cdot[C_{j+y}]} \tag{16}$$

$$= p^{-(i+j)}[\phi(i,j)]. \tag{17}$$

For a high-molecular-weight mixture, p(the extent of reaction of linear species)$\approx$*1 and* $\Delta H\approx 0$ are approximated. Substituting Eq. 15 to Eq. 17, then we obtain

$$\begin{aligned} [\phi(i,j)] \approx \Phi\cdot P\cdot E\cdot\{V^2/\sigma_{R_i}\cdot\sigma_{R_j}\cdot N_A^2\}\cdot \\ W_i(\mathbf{0})\cdot W_j(\mathbf{0}). \end{aligned} \tag{18}$$

Rearranging Eq. 18, we have an expression for the quantity of $\phi(i, j)$:

$$\begin{aligned} [\phi(i,j)] &\approx \Phi\cdot P\cdot E\cdot\{V\cdot W_1(\mathbf{0})/\sigma_{R_i}\cdot N_A\} \\ &\times\{V\cdot W_j(\mathbf{0})/\sigma_{R_j}\cdot N_v\} \qquad (19) \\ &\equiv \Phi\cdot P\cdot E\cdot[R_i][R_j] \quad (\text{mole/V}). \qquad (19') \end{aligned}$$

The physical meaning that Eq. 19 suggests is easy to

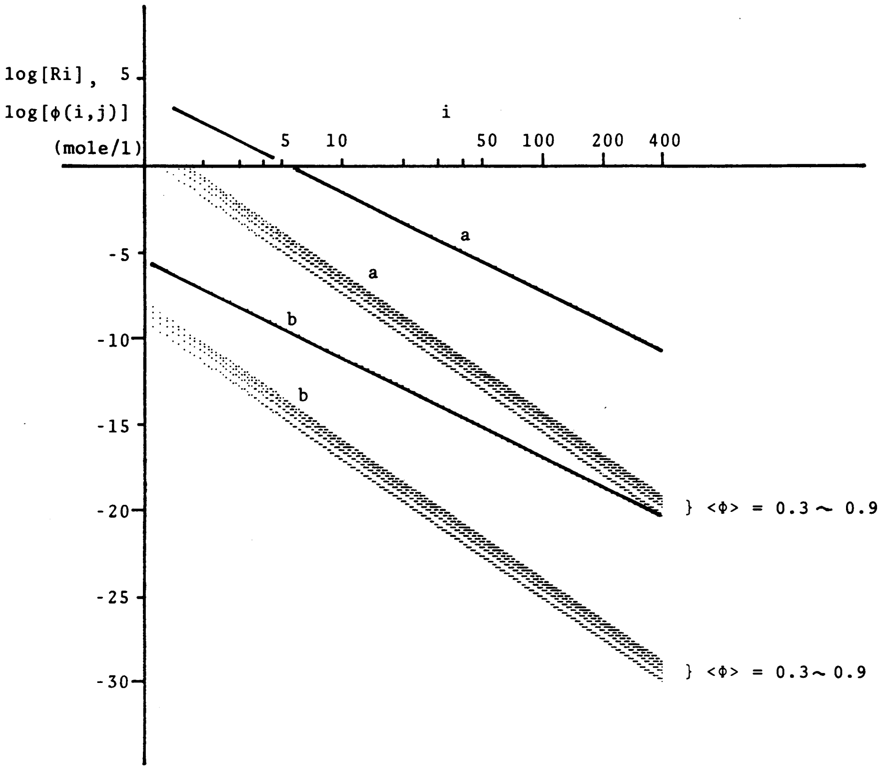

Fig. 1. Catenane distribution (broken lines) from $i=j$ rings compared to ring distribution (solid lines) for Kuhn segment number.
a: Kuhn segment length, $l=2$. b: $l=50$. Each four curves from $\langle\Phi\rangle=0.3$ to 0.9 (step 0.2) are drawn.

Table 1. The Equilibrium Constant of the Catenation between 186 DNA and $\lambda_c I_{857}$DNA

Experimental	Wang & Schwartz	Suematsu & Ogura
$K = 2.2 \times 10^{-13}$ cm^3	7.8×10^{-13}	3.5×10^{-13}

comprehend: i.e., the quantity of the catenane $\phi(i, j)$ is proportional to the product of the concentrations of cyclic i and j-mer, and the probability for the entanglement of both.

In terms of the weight fraction $X_{\phi(i,j)}$, Eq. 19 leads to

$$X_{\phi(i,j)} \simeq \Phi P E \frac{(i+j)}{i \cdot j} C_0 X_{Ri} X_{Rj}, \tag{20}$$

where C_0 is the initial monomer concentration.

Discussion

As is clear from Eq. 20, the probability that catenation occurs is proportional to the product of the cyclization probabilities of rings i and j, suggesting that catenanes will be formed only with a very low probability, especially for larger i and j.

Letting n be the segment number, since P varies roughly as $n^{3/2}$ and X_{Rn} as $n^{-3/2}$, $X_{\phi(i,j)}$ must decrease in proportion to $n^{-5/2}$. Thus, the catenane from macrocyclics may be neglected (Fig. 1).

E may be unity in θ points or above the critical concentration C^* defined by $\psi_{\text{in}} = \psi_{\text{out}}$. Finally, Eq. 19 is reduced to a conclusion analogous to previous reports[1,5]:

$$[\phi(i,j)] \simeq \Phi\left(\frac{4}{3}\pi S^3 \frac{N_A}{V}\right)[R_i][R_j]. \tag{21}$$

One credible example has been reported for catenation; i.e., dimeric catenanes between 186 DNA and $\lambda_c I_{857}$DNA are formed to yield $K = 2.2 \times 10^{-13}$ cm^3.[5]

Adopting as a value of s the sum of the radiuses of gyration of the rings and $\langle\Phi\rangle \simeq 0.4$—$0.6$, a better agreement between theory and experiment is found (Table 1) (see Appendix I).

Appendix I

For an extreme rigid(thin) chain, the catenation probability is given by[3]

$$\Phi \cong A \exp(-\alpha s^3).$$

A and α are the constants for the given Kuhn segment number. Then, the average value of Φ may be written

$$\langle\Phi\rangle = \int_0^s 4\pi s^2 \Phi \, ds \Big/ \int_0^s 4\pi s^2 \, ds.$$

A numerical calculation yields $\langle\Phi\rangle \cong 0.33$ for $n=20$, 0.37 for $n=40$, 0.41 for $n=60$ and 0.43 for $n=80$ (increasing slowly with chain length). It seems to be in a rough linear relationship to the logarithm of the segment number in this range, i.e.,

$$\langle\Phi\rangle \sim \operatorname{Log} n.$$

Thus, $\langle\Phi\rangle \cong 0.4$—$0.6$ is a good approximation for $n \cong 200$ in DNA.

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