Concentration Invariance of Cyclic Species

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Abstract
We examine the concentration invariance of cyclic species for the irreversible polymerization. The simulation results show that the invariance holds in good approximation in the irreversible process also. The validity of the simulation equations employed was confirmed through comparison with the recent experimental observations by the Nagoya university group carried out independently of the present work.

Key Words: Numerical Solution/ Distribution of Cyclic Species/ Concentration Invariance

1 Introduction
It has been well established that the relative frequency of ring formation to intermolecular reaction increases with dilution. It was pointed out, on one hand, that the ring concentration is independent of the monomer concentration. This feature has been proven rigorously for the reversible difunctional system [1]. In this paper we examine the irreversible polymerization [2] to prove that the concentration invariance of cyclic species is satisfied for the irreversible case also. The soundness of the result is confirmed through comparison with the recent experimental observation of the telechelic polystyrene by the Nagoya university group [3].

2 Theoretical
Let $M_0$ be the initial monomer number and $V$ the system volume. The birth-death equation for the AA-type difunctional polymerization can be expressed in the form:

$$
\frac{\delta N_x}{\delta u} = \frac{2 \sum_{j=1}^{x-1} N_j N_{x-j}}{2(M_0 - u)^2 + V \sum_k \varphi_k N_k} - \frac{4N_x(M_0 - u) + V \varphi_x N_x}{2(M_0 - u)^2 + V \sum_k \varphi_k N_k}, \quad (1)
$$

$$
\frac{\delta N_{Rx}}{\delta u} = \frac{V \varphi_x N_x}{2(M_0 - u)^2 + V \sum_k \varphi_k N_k}, \quad (2)
$$

where $N_x$ and $N_{Rx}$ denote the numbers of chain $x$-mers and cyclic $x$-mers respectively ($x = 1, 2, \cdots$ being the number of repeating units), $u$ the number of unit reactions ($u = 0, 1, 2, \cdots$), and $\varphi_x$ the relative cyclization frequency [1]. For the bifunctional system $u$ is equal to the number of bonds.

The quantity $\varphi_x$ is defined by $\mathcal{P}/v$ where $\mathcal{P}$ is the probability that one end on a linear $x$-mer chain enters the small volume $v$ with the radius $\epsilon$ around the another end. For the Gaussian chain $\varphi_x$ has the form:

$$
\varphi_x = \left( \frac{d}{2\pi^{d/2} \ell_s^d N_A} \right) \int_0^{d/2\nu_x} t^{d-1} e^{-t} dt, \quad (3)
$$

where $d$ is the space dimension, $N_A$ the Avogadro number and $\nu_x$ the quantity defined by

$$
\nu_x = \langle r_x^2 \rangle / \ell_s^2, \quad (4)
$$

where $\langle r_x^2 \rangle$ is the end-to-end distance. In poor solvents, or in the limit of infinite concentration ($C \rightarrow \infty$), the excluded volume effect is expected to vanish and then

$$
\nu_x = \langle r_x^2 \rangle \phi / \ell_s^2 = C_F \xi \nu_x \quad (4')
$$
with the subscript $\Theta$ signifying the Flory unperturbed state, $C_F$ the Flory characteristic ratio, and $\xi_e$ the effective bond number within a repeating unit defined by $\xi_e = \frac{1}{\ell_s^2} \sum_i \ell_i^2$. Note that $C_F$ is not a constant, but an increasing function of $x$ and approaches a constant as $x \to \infty$.

Contrary to the ideal system without rings, there is no explicit closed solution [1] for the above equations, so $N_x$ or $N_{R_x}$ cannot be expressed uniquely in terms of $u$. Fortunately, eqs. (1) and (2) can be solved numerically [2]. Chemical reactions are by nature discrete, because the number of events is enumerable. Thus these equations are essentially recursive.

To solve eqs. (1) and (2), it is convenient to sum up the above equations from $u = 0$ to $p$ (an arbitrary number of events) to obtain

$$N_x(p) = \sum_{u=0}^{p-1} \left\{ \frac{2 \sum_{j=1}^{u-1} N_j(u) N_{x-j}(u)}{2(M_0-u)^2 + V \sum_{k=1}^{\infty} \varphi_k N_k(u)} - \frac{4N_x(u)(M_0-u) + V \varphi_x N_x(u)}{2(M_0-u)^2 + V \sum_{k=1}^{\infty} \varphi_k N_k(u)} \right\}$$

with the boundary conditions:

$$N_x(0) = \begin{cases} 0 & \text{if } x \neq 1 \\ M_0 & \text{if } x = 1, \end{cases} \quad N_{R_x}(0) = 0 \quad \text{for all } x's.$$

Table 1: Model polymerization of the telechelic polystyrene in THF

| parameter                     | symbol | value            |
|-------------------------------|--------|------------------|
| molecular weight              | $M_W$  | $4.6 \times 10^4$ |
| characteristic ratio          | $C_F$  | 10               |
| expansion factor              | $\alpha$ | 1.39             |
| effective bond number         | $\xi_e$ | 867              |
| standard bond length (Å)      | $\ell_s$ | 1.55             |
| monomer concentration (mol/l) | $C_0$  | $2 \times 10^{-4}$ |

Let us perform the calculation of the above equations modeling the polymerization of the telechelic polystyrene (t-PS: $M_W = 4.6 \times 10^4$, $\bar{x} = 440$) in tetrahydrofuran (THF) as a good solvent with the help of the parameters shown in Table 1 [3]. We assume the Gaussian behavior of the polystyrene chain having the expansion factor $\alpha = 1.39$, i.e., the Gaussian chain having the end-to-end distance $(\bar{r}^2) = \alpha^2 (\bar{r}_s^2)$. The simulation was performed to calculate the weight average distribution for $D = 0.84$ (Fig. 1) and the limiting case of $D \to 1$ (Fig. 2), where $D$ is the extent of the advancement of reaction defined by $D = u/M_0$.

In Fig. 1 solid lines represent the theoretical curves based on eqs. (5) and (6) ($D = 0.84$ is assumed) for cyclic and acyclic species, respectively, and diamonds (♦) and crosses (×) are corresponding experimental observations by Kushida and coworkers [3] under the same reaction condition. Agreement between the theory and the experiments is amazingly good. This convinces us the soundness of the kinetic formulas (5) and (6).

From Fig. 2, one can see that the concentration of rings ([Γ]) has the Γ-line curve which was already observed in the equilibrium polymerization (see Remark 1): i.e., there is a plateau zone in high concentration where $\Gamma \to \infty$ corresponds to $\geq 0.1$ w/v %.

![Fig. 1: Experimental weight fractions of cyclic (♦) and acyclic species (×) in the polymerization of the telechelic polystyrene monomer (MW = 46000) (Results from Kushida and coworkers [3]). Solid lines (−): theoretical lines at $D = 0.84$ by eqs. (5) and (6).](image-url)
\([\Gamma]\) is approximately constant over broad monomer concentration \((C_0)\) range, whereas in the low concentration of \(C_0 \lesssim 10^{-3}\ \text{mol/l}, \ [\Gamma]\) decreases strongly with increasing dilution along with the sudden rise of the weight fraction \(w_R\) of rings. The upper bound of \(C_0 \approx 0.02\) in Fig. 2 corresponds to the non-solvent system. The strong rise of \(w_R\) in the low concentration indicates that the ring formation begins to overwhelm the intermolecular reaction, in which the production of large molecules is no longer possible because the molecular growth occurs only through intermolecular linking.

As shown earlier, eqs. 5 and 6 has the limiting solution of \(C_0 \rightarrow \infty:\)

\[ [\Gamma]_{C_0 \rightarrow \infty} = \sum_{x=0}^{\infty} \varphi_x \frac{D^x}{2x} \]

As \(D \rightarrow 1\), eq. (7) leads to

\[ [\Gamma]_{C_0 \rightarrow \infty} \rightarrow \sum_{x=0}^{\infty} \varphi_x \frac{1}{2x} \]

The dotted line in Fig. 2 illustrates this eq. (8). One can see that there is slight numerical difference in the plateau zone between \([\Gamma]\) of the present simulation (solid line) and that of eq. (8) (dotted line). There is also observed substantial difference in quality of the concentration invariance of \([\Gamma]\) between the irreversible case (Fig. 2) and the reversible case (Fig. 3). The differences is (probably) due to the small sample space \((M_0 = 100)\) employed in this simulation. The essential feature is, however, quite alike, namely, \([\Gamma]\) is almost constant over broad concentration range. Thus one can apply the invariance principle to the irreversible polymerization process without introducing an appreciable error to our final results [1].

An important question is whether one can extend the principle of the concentration invariance of cyclic species to a more general case of \(f \geq 3\) [1]. At present a rigorous proof does not appear available. From the chemical dynamics point of view, however, the two systems (linear and branching) have exactly the same feature that the molecular growth occurs through the competition between the intermolecular reaction and the cyclization of linear molecules (see Fig. 3). In this sense, no difference exists between the linear system and the branching system: one may regard every reaction in a branched system as a reaction of a chain molecule (cyclization) or between chain molecules (intermolecular reaction) embedded on clusters. In fact we can describe the ring-forming process of the branching system by the formula precisely identical with that of the linear system:

\[ \delta \sum_{x=1}^{\infty} N_{R_x} = \sum_{x=1}^{\infty} \left( \frac{v_{R_x}}{v_L} \right) \frac{\varphi_x}{1 + \sum_1^{\infty} \left( \frac{v_{R_x}}{v_L} \right)} \delta u. \]

For a large \(C_0\), it follows that \(\sum_x \left( \frac{v_{R_x}}{v_L} \right) \ll 1\), and the above equation yields the known limiting solution: for instance, \(\sum_x \varphi_x [ (f-1)D ]^x / 2x \) for the R-A\(_f\) model [1].

The solution is independent of \(C_0\), which convinces us strongly the principle of the concentration invariance of the cyclic production for the branching process.

### 3 Possibility of Experimental Verification of the Concentration Invariance

Let \(\Omega\) denote the total number of molecules in a given branching system and \(\Omega_0\) the corresponding quanity in the ideal system with no rings. Following the known relation, we write as:

\[ \Omega - \Omega_0 = \Gamma, \]

while

\[ X_n = M_0/\Omega \]

\[ \Omega_0 = M_0(1 - \frac{1}{2}fD) \]
where $X_n$ is the number average molecular weight. Eq. (10) is a universal relation valid for all bond forming processes within the interval $0 \leq D \leq D_c$. Substituting eqs. (11) and (12) into eq. (10) and using the relation $C_0 = M_0/V$ and $[\Gamma] = \Gamma/V$, one has the equality:

$$[\Gamma] = C_0 \left( \frac{1}{X_n} - 1 + \frac{1}{2} f D \right).$$

(13)

The conclusion of eq. (13) is important. It states that if $X_n$ can be measured experimentally as a function of $D$ and $C_0$, one can estimate $[\Gamma]$ as a function of $C_0$. This provides a possibility that one can test experimentally the assumption of the concentration invariance of $[\Gamma]$ for general branching processes of $f \geq 3$. This possibility was first suggested by Faliagas [4]. To apply eq. (13), it can be conveniently recast in the form:

$$X_n = \frac{1}{[\Gamma]/C_0 + 1 - \frac{1}{2} f D}.$$

(14)

From Fig. 2, the term $(1 - \frac{1}{2} f D)$ is of the order $\approx 0.01$, while the quantity $[\Gamma]/C_0$ is of the order $\approx 10^{-3}$. Hence the effect of the ring formation on $X_n$ is experimentally measurable.

### 4 Conclusion

The present simulation showed that the concentration invariance is well satisfied for the irreversible difunctional polymerization. There exist some reasons to consider that this principle applies to the branching process also; for instance, (i) the limiting solution is independent of $C_0$; (ii) no inconsistency has been found up to present for the theory of gelation constructed on the basis of this invariance principle [1]. There is a possibility to prove directly the concentration invariance of cyclic species through the relationship of eq. (14).

### Appendix

It will be useful to compare the result in the text with the equilibrium case [1]. Assume an imaginary case in which the above-mentioned PSt undergoes the equilibrium polymerization. The corresponding equilibrium solution is of the form:

$$[\Gamma] = \sum_{x=0}^{\infty} \varphi_x \left( \frac{D - w_R}{1 - w_R} \right)^x/2^x,$$

(15)

so that

$$C_0 = \frac{1}{w_R} \sum_{x=0}^{\infty} \varphi_x \left( \frac{D - w_R}{1 - w_R} \right)^x/2.$$

(16)

We show below a special case of $D \to 1$.

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Fig. 4: Total concentration $[\Gamma]$ and weight fraction $w_R$ of cyclic species in equilibrium polymerization as against initial monomer (PSt) concentration $C_0$. Fig. 4-(B) is a magnification of Fig. 4-(A). The arrows (↑) in Fig. 4-B indicate the critical concentration, $C_0^*$, below which the concentration invariance of cyclic species breaks down.
As one can see, there is a clear-cut critical point, $C_0^*$, below which the concentration invariance of $[\Gamma]$ breaks down. From eq. (16), it follows that $C_0^* = \sum_{x=0}^{\infty} \varphi_x / 2$. For $C_0 \leq C_0^*$, the weight fraction of rings, $w_R$, is held unity, while $[\Gamma]$ decreases with dilution; first slowly, then rapidly, and finally as $[\Gamma] = C_0$, showing that the monomeric ring occurs more abundantly with dilution and exclusively in the limit of $C_0 \to 0$.

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