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Communication to the editor. Comments on the paper ‘combinatory entropy in complex polymer solutions’ by Susumu Saeki, polymer, 2000;41:8331

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Susumu Saeki has contributed much [1–4] to better understanding the nature of combinatory entropy for polymeric systems and to designing procedures to calculate it. In particular, he has derived this quantity for the star-shaped polymer—low-molecular-weight liquid (LMWL) in comparison with a similar system with the corresponding linear polymer of the same molecular mass [4]. Saeki’s formula predicts that the polymer critical concentration ϕ_{2c} will increase and the critical temperature T_c will decrease on switching from the linear topology to the star-shaped one, but it overestimates the predicted effect relative to the effect observed experimentally. For example, Yokoyama et al. [5] report a rise of ϕ_{2c} from 0.03 to 0.04 when linear polystyrene (molecular mass $M=1.2\times10^6$) is replaced by star-shaped polystyrene (average arm number 6.3) in a mixture with cyclohexane, while Saeki’s formula gives a $0.031\rightarrow0.072$ increase. In a previous paper [6] we have estimated the calculated shift in T_c in a similar case ($M=2.05\times10^6$, 11 arms) and have gotten about 17 K against the experimental value of 3 K. This was the very reason we had to reject Saeki’s formula and retain the formula for linear polymer (as a first approximation); as a result, the shift of both critical point and binodal as a whole was explained in terms of a modification of the enthalpy of mixing (the Okada–Numasawa model [7]).

In this connection, it seems reasonable to verify Saeki’s formula for internal consistency. Saeki [4] treats an r-segment star-shaped macromolecule consisting of a central segment and n arms of x segments each ($r=nx+1$). The intramolecular contribution into the partition function is

$$q_2=\left[(x+1)\left(\frac{z-1}{e}\right)^x\right]^n=(x+1)^n\left(\frac{z-1}{e}\right)^{r-1} \tag{1}$$

where z is the coordination number of the lattice. For a linear flexible-chain polymer this quantity is (Saeki [2])

$$q_2=\frac{z(z-1)^{r-2}r}{e^{r-1}} \tag{2}$$

When $n=1$, Eqs. (1) and (2) coincide, since a one-arm star is actually a linear chain. However, these equations must also coincide at $n=2$ as a two-arm star is obviously a linear chain as well. Then $x=(r-1)/2$ and $(x+1)^n=(r/2+1/2)^2\neq r$ when $r\neq1$. Hence, Saeki’s formula for the intramolecular component does not stand this test.

True, this component does not contribute to the entropy of mixing but the intermolecular term also seems incorrect. Saeki [4] assembles a star from n linear chains of $(x+1)$ segments each and states that $(n-1)$ end segments disappear. He concludes from this that the probability P of selecting the correct polymer configurations switches from ϕ_2^{r-1} to $\phi_2^{(r-1)-(n-1)}=\phi_2^{r-n}$. But the disappearance of $(n-1)$ segments alone does not mean the appearance of a star (this is a necessary but insufficient condition). Moreover, this does not mean that n linear chains produce a macromolecule with any architecture. In fact, the author himself notes that the entropy of mixing of a star-shaped macromolecular solution is, surprisingly, equal to that of a disconnected arm solution.

Let us calculate the number of ways the $(i+1)$th star-shaped macromolecule can be placed on a lattice of $N=N_1+rN_2$ sites (N_1 and N_2 being the number of LMWL molecules and macromolecules, respectively) again in the spirit of the original Flory–Huggins theory [8]. The central segment can be put on any of the $(N-ir)$ free sites. Then the first arm is to be placed: its first segment has $z(1-ir/N)$ sites to occupy, any other segment has $(z-1)(1-ir/N)$ ones.

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Multiplying, we obtain:

$$(m - zi)z(z-1)^{x-1}\left(1 - \frac{ir}{N}\right)^{x}$$

Return to the centre and place the second arm. Its first segment has $(z-1)(1-ir/N)$ sites to be placed at (since some sites around the centre are already occupied), each other segment has the same number of variants. So, the second arm can be placed in $(z-1)^x(1-ir/N)^x$ ways.

We now return to the centre again. It is obvious that the only distinction between the arms is in the number of possible ways to place the first segment, which varies from $z(1-ir/N)$ to $(z-n+1)(1-ir/N)$, where the first factor sequentially reduces by 1. The overall number for the $(i+1)$ th star is derived by multiplication:

$$\begin{aligned}\beta_{i+1} &= (N - ir)z(z-1)\ldots(z-n+1)\\ &\quad\times(z-1)^{n(x-1)}\left(1-\frac{ir}{N}\right)^{nx}\\ &= \frac{z!}{(z-n)!}\,\frac{(N-ir)^r(z-1)^{r-n-1}}{N^{r-1}}\\ &= \frac{(N-ir)^r(z-1)^{r-1}}{N^{r-1}}\,\frac{z!}{(z-1)^n(z-n)!}\end{aligned}$$

The first fraction here is β_{i+1} for a linear chain and the second one is a correction for the star-shaped topology and, following common transformations, enters the intramolecular component only:

$$q_2 = \frac{z!(z-1)^{r-1-n}r}{(z-n)!e^{r-1}}$$

Unlike Eq. (1), this formula coincides with Eq. (2) at $n=2$ as well as at $n=1$. But the intramolecular component does not affect the entropy of mixing while the intermolecular component remains as in the case of linear chains. Hence, the entropy of mixing remains unaffected at the linear-to-star-shaped topology switch.

The same placing procedure (with multiple returns) applies to comb-shaped macromolecules and those of any other topology, the only quantity to be changed is the number of ways the first segment of every new arm treated can be placed. This will affect the intramolecular component, and the entropy of mixing will remain unchanged.

This conclusion explains a fair fit of the binodals of the star-shaped polystyrene—cyclohexane system in terms of a modified expression for the enthalpy of mixing [6,7].

Thus, by considering the direct placing procedure with multiple returns to middle segments, we can draw the global conclusion that the combinatory entropy of mixing of a flexible-chain polymer with LMWL is independent of the macromolecular architecture. The effect of any change in the molecular topology should be associated with either the non-combinatory contribution to the entropy or the enthalpy of mixing.

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