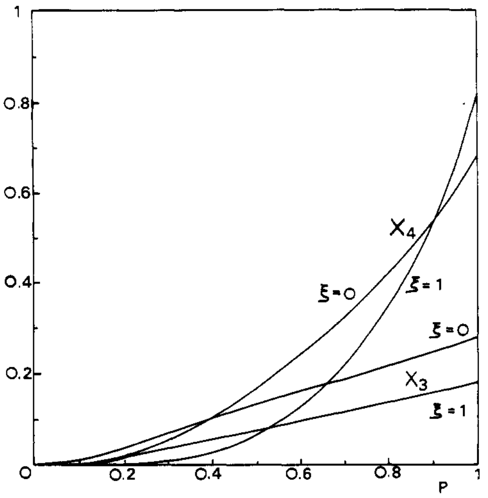

Figure 3. Fraction of A_4 molecules belonging to the polymer, with three (X_3) and four (X_4) arms going to the gel, as a function of reaction extent, for the two limiting cases of $\xi = 0$ (termination by chain transfer and/or disproportionation) and $\xi = 1$ (termination by combination).

bination leads to $X_3 = 0.177$ and $X_4 = 0.812$, while termination by chain transfer and/or disproportionation leads to the following values: $X_3 = 0.276$ and $X_4 = 0.679$. Thus, it may be reasonably expected that both types of networks will show different macroscopic properties. For example, it may be inferred that, due to the increase in the overall concentration of cross-linking points ($X_3 + X_4$) as well as in the relative amount of X_4 with respect to X_3, both the rubbery elastic modulus and the glass transition temperature will be higher for a network where termination takes place by combination (when compared with the same network with termination taking place by chain transfer and/or disproportionation).

Conclusions

By use of a fragment approach, statistical parameters of networks built up by a free-radical mechanism could be obtained both in pre- and postgel stages. This analysis introduces the effect of the nature of the termination mechanism on the network structure. When the termination mechanism is shifted from chain transfer and/or disproportionation to combination, gelation is advanced by a factor of 2/3, the amount of soluble material in the polymer fraction decreases, and the amount of elastic material in the polymer increases while showing a higher concentration of the cross-linking units with the highest possible functionality. It may, then, be inferred that a change in termination mechanism will be associated with variations in the macroscopic properties of the resulting network.

Registry No. Methyl methacrylate, 80-62-6; ethylene dimethacrylate, 97-90-5.

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Effect of Short-Range Correlation between Chain Elements on the Hydrodynamic Radius and the First Cumulant in Dilute Polymer Solutions

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ABSTRACT: It was checked how the first cumulant Ω and the hydrodynamic radius R_H of polymer dynamics in dilute solutions *in good solvent limit* were influenced by short-range correlation between the chain elements. For a scaling form of the element distribution and Oseen hydrodynamic interaction in the Kirkwood scheme, Ω at the q^3 regime was not affected by the short-range correlation, but R_H at smaller q was strongly affected. This result might indicate (1) an inadequacy of the Oseen description of hydrodynamic interaction in the Kirkwood formula and/or (2) the approximate nature (or a lack of accuracy) of the Kirkwood formula.

Introduction

The translational diffusion coefficient D (or the equivalent hydrodynamic radius R_H) and the first cumulant Ω of a single flexible polymer chain in dilute solutions have been made experimentally clear by dynamic light-scattering spectroscopy in wide ranges of the scattering vector (q) and the molecular weight.[1] It has recently been revealed that in the highly swollen state these characteristics were in apparent agreement with those of the nondraining Gaussian chain model with nonpreaveraged Oseen hydrodynamic interaction, i.e., the characteristic ratio R_H/R_G and the reduced first cumulant $\Omega/(q^3 k_B T/\eta_0)$ were very close to the theoretical values in the unperturbed chain state.[2] Here R_G is the static radius of gyration of the polymer. However, this agreement is very curious since the element distribution in the swollen chain is not Gaussian at all. Use of the realistic element distribution,[3a] where the small-distance behavior is taken into consideration by a scaling form, may help this curious situation. In this paper, we investigate effects of the short-range correlation between chain elements on R_H and Ω through the scaling form.

Calculation and Results

According to the Akcasu–Gurol[4] treatment based on the general diffusion theory of Kirkwood,[5] the Ω of a chain

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composed of N scattering elements is given, in the form of Fixman,[6] by

$$\Omega = \sum_j^N \sum_k^N \langle (\mathbf{q}\cdot\mathbf{D}_{jk}\cdot\mathbf{q}) \exp(i\mathbf{q}\cdot\mathbf{r}_{jk})\rangle / \sum_j^N \sum_k^N \langle \exp(i\mathbf{q}\cdot\mathbf{r}_{jk})\rangle \quad (1)$$

where $\mathbf{D}_{jk}$ is a component of the diffusion tensor and is described by the Oseen formula

$$\mathbf{D}_{jk} = k_BT[\delta_{jk}\zeta_j^{-1}\mathbf{1} + (1-\delta_{jk})(8\pi\eta_0 r_{jk})^{-1}(\mathbf{1} + r_{jk}^{-2}\mathbf{r}_{jk}\mathbf{r}_{jk})] \quad (2)$$

where ζ_j is the friction coefficient for element j, η_0 is the solvent viscosity, and $\mathbf{r}_{jk}$ is the vector from element j to element k. The angular brackets denote the averages over the *equilibrium* distribution. The denominator of eq 1 is equal to $N^2P(q)$, where $P(q)$ is the particle scattering function. For linear nondraining chains without preaveraged hydrodynamic interaction, the off-diagonal elements in eq 2 is only concerned. The expression of the numerator in eq 1 gives the advantage that the Oseen tensor need not always be *preaveraged* over the equilibrium distribution, as it is replaced by the approximation

$$\Omega_{\text{pre}} = \sum_j^N \sum_k^N \langle \mathbf{q}\cdot\mathbf{D}_{jk}\cdot\mathbf{q}\rangle \langle \exp(i\mathbf{q}\cdot\mathbf{r}_{jk})\rangle / N^2P(q) \quad (3)$$

In the calculation of eq 1, we take an average first over all orientations[7] and then over scalar distance r_{jk} by using a realistic distribution, i.e., a generalized Domb–Gillis–Wilmers form.[3] This distribution can be expressed by the function of r ($\equiv r_{jk}$) and n ($\equiv |j-k|$) as

$$W(r,n) = \{t/\sigma_n^{l+1}\Gamma[(l+1)/t]\}r^l \exp[-(r/\sigma_n)^t] \quad (4)$$

with $\sigma_n^2 = \langle r_n^2\rangle\Gamma[(l+1)/t]/\Gamma[(l+3)/t]$, $\langle r_n^2\rangle = An^{2\nu}$, and $t = 1/(1-\nu)^8$ at $2 \le t \le 2.5$. Here $\Gamma(u)$ is the Γ function and $\langle r_n^2\rangle$ the mean-square end-to-end distance of a polymer consisting of n elements. A is a numerical constant, and l and t are critical exponents related to the short-range correlation between elements.[9] The form of W in eq 4 is possessed of the scaling nature shown by des Cloizeaux[9] and de Gennes:[10]

$$W_i(r,n) \propto n^{-d\nu}f^{(i)}(r/n^\nu) \quad (5)$$

$$f^{(i)}(z) \propto z^{\Theta_i} \qquad (z \ll 1)$$

$$f^{(i)}(z) \propto \exp(-z^{t_i}) \qquad (z \gg 1)$$

where d is the spatial dimensionality. The elements j and k are both on the end points of the chain for the case $i = 0$, one on the end point and the other on the interior for the case $i = 1$, and both on the interior for the case $i = 2$. Comparison between eq 4 and 5 for $d = 3$ gives that $l \equiv l_i = 2 + \Theta_i$ and $t = t_i$. The exponent l_i gives a measure of the strength of the excluded volume interaction at short ranges, and the initial slope of W at small r is expected to decrease as i increases; theoretical values are $l_0 = 2.273$, $l_1 = 2.459$, and $l_2 = 2.71$[9a,11] for $d = 3$, while t_i is roughly independent of i for $d = 3$; $t_0 = 2.5$[3b,8] or 2.427,[9b] and $t_1 = 2.6$.[11]

Converting the double sum in eq 1 to integrals, we have

$$\sum_{j,k}^N \langle (\mathbf{q}\cdot\mathbf{D}_{jk}\cdot\mathbf{q}) \exp(i\mathbf{q}\cdot\mathbf{r}_{jk})\rangle = (q^3k_BT/2\pi\eta_0)(N^2/\nu\Gamma[(l+1)/t])\int_0^\infty (u^{-2}\sin u + u^{-3}\cos u - u^{-4}\sin u)[f_1(u) - f_2(u)]\,du \quad (6)$$

$$N^2P(q) = \{2N^2/\nu\Gamma[(l+1)/t]\}\int_0^\infty (u^{-1}\sin u)[f_1(u) - f_2(u)]\,du \quad (7)$$

with

$$f_s(u) = y^{-s/\nu}u^{s/\nu-1}\Gamma[(l+1-s\nu^{-1})/t,\ (u/y)^t] \qquad (s = 1, 2) \quad (8)$$

Here $u = qr_{jk}$, $y = \sigma_N q$, and $\Gamma(a,b)$ is the incomplete Γ function.

At large qR_G, i.e., $y \to \infty$, the incomplete Γ functions can be approximated by the complete ones. Therefore, after tedius integrations of eq 6 and 7 by parts, we can obtain

$$\lim_{q\to\infty} \sum_{j,k}^N \langle (\mathbf{q}\cdot\mathbf{D}_{jk}\cdot\mathbf{q}) \exp(i\mathbf{q}\cdot\mathbf{r}_{jk})\rangle / (q^3k_BT/\eta_0) = N^2\{4\nu\Gamma[(l+1)/t]\}^{-1}\{y^{-1/\nu}\Gamma[(l+1-\nu^{-1})/t][-\cos(\pi/2\nu)]^{-1}[1/\Gamma(3-\nu^{-1}) - 1/(\nu^{-1}-2)(\nu^{-1}-4)\Gamma(2-\nu^{-1})] - y^{-2/\nu}\Gamma[(l+1-2\nu^{-1})/t][\cos(\pi/\nu)]^{-1}[2(\nu^{-1}-1)/\Gamma(4-2\nu^{-1}) - 1/\Gamma(5-2\nu^{-1})]\} + \text{remainder} \qquad (\tfrac{1}{2} < \nu \le \tfrac{3}{5}) \quad (9)$$

$$\lim_{q\to\infty} N^2P(q) = 2N^2\{\nu\Gamma[(l+1)/t]\}^{-1}\{y^{-1/\nu}\Gamma[(l+1-\nu^{-1})/t]\Gamma(\nu^{-1}-1)\sin[\pi(\nu^{-1}-1)/2] + y^{-2/\nu}\Gamma[(l+1-2\nu^{-1})/t](2\nu^{-1}-2)(2\nu^{-1}-3)\Gamma(2\nu^{-1}-3) \times \sin[\pi(2\nu^{-1}-3)/2]\} + \text{remainder} \qquad (\tfrac{1}{2} \le \nu \le \tfrac{3}{5}) \quad (10)^3$$

Taking the terms containg $y^{-1/\nu}$ only, we finally obtain

$$\lim_{q\to\infty} \Omega/(q^3k_BT/\eta_0) = [1/8\Gamma(\nu^{-1}-1)][1/\cos(\pi/2\nu)]^2\{1/\Gamma(3-\nu^{-1}) - 1/(\nu^{-1}-2)(\nu^{-1}-4)\Gamma(2-\nu^{-1})\} \qquad (\tfrac{1}{2} < \nu \le \tfrac{3}{5}) \quad (11)$$

From eq 6 with $\nu = {}^1/_2$, we have the asymptotic Ω value with a nonpreaveraged Oseen tensor in Θ solvent, $\lim_{q\to\infty} \Omega_\Theta/(q^3k_BT/\eta_0) = {}^1/_{16} = 0.06250$, which is frequently quoted by many workers.[7,12] Unexpectedly, the effect of the excluded volume interaction at short ranges on Ω *does disappear* in eq 11 and $\lim_{q\to\infty} \Omega/(q^3k_BT/\eta_0)$ depends only on ν. This result is distinct from the Ω value at large qR_G with a *preaveraged* Oseen tensor:

$$\lim_{q\to\infty} \Omega_{\text{pre}}/(q^3k_BT/\eta_0) = (t/12l)\{\Gamma[l/t+1]/\Gamma[(l+1)/t]\} \times \{\Gamma[(l+2-\nu^{-1})/t]/\Gamma[(l+1-\nu^{-1})/t]\}\{\Gamma(3-\nu^{-1}) \times \Gamma(\nu^{-1}-1)\cos^2(\pi/2\nu)\}^{-1} \qquad (\tfrac{1}{2} \le \nu \le \tfrac{3}{5}) \quad (12)$$

which depends not only on ν but also t and l.

In contrast, the ratio R_G/R_H depends strongly on the short-range feature, as described below. The Stokes radius R_H is related to the translational diffusion coefficient, which is observable at sufficiently small q, as

$$D = \lim_{q\to 0} q^{-2}\Omega = (qN)^{-2}\sum_{j,k}^N \langle \mathbf{q}\cdot\mathbf{D}_{jk}\cdot\mathbf{q}\rangle = (k_BT/6\pi\eta_0)(\sum_{j\ne k}^N \langle r_{jk}^{-1}\rangle/N^2) \equiv (k_BT/6\pi\eta_0)R_H^{-1} \quad (13)$$

This is precisely the Kirkwood equation for D (ref 5) and shows that R_H is not affected by preaveraging the Oseen tensor.[7,12] For the distribution of eq 4, we have

$$R_G/R_H = \{\Gamma[(l+3)/t]/2(1+\nu)(1+2\nu)\Gamma[(l+1)/t]\}^{1/2}\{2\Gamma(l/t)/(1-\nu)(2-\nu)\Gamma[(l+1)/t]\} \quad (14)$$

which depends on l as well as t and ν but not on N.

Discussion

For highly swollen chains, a set of $\nu = 0.5830$, $t = 2.398$, and $l = 2.802$ was reported by Tsunashima and Kurata (TK).[3a] The values are close to the theoretical ones $\nu =$

Table I
First Cumulant and Characteristic Ratios for Sets of Critical Exponents ν, t, and l

			$\lim_{q\to\infty} \Omega/(q^3k_BT/\eta_0)$			
ν	t	l	non-PA[a]	PA	R_G/R_H	remarks
0.5830	2.398	2.802	0.075 38	0.076 38	1.596	TK[3a]
0.5880	2.427	2.71[b]				LG–ZJ[13]
0.6	2	2	0.078 76	0.071 04	1.860	pseudo-Gaussian
0.5	2	2	0.062 50	0.053 05	1.505	Gaussian
experimental			0.0616		1.50	PIP–good solvent[c]
			0.048		1.30	PIP–Θ solvent[c]

[a] PA = preaveraged Oseen tensor. [b] des Cloiseaux second-order ϵ expansion.[9a] [c] Polyisoprene in a good solvent (cyclohexane)[2] and in a Θ solvent (1,4-dioxane).[21]

0.5880 and $t = (1 - \nu)^{-1} = 2.427$ by Le Guillou and Zinn-Justin[13] and to the second-order ϵ-expansion value $l_2 = 2.71$ by des Cloizeaux.[9a] The TK set gives 0.0754 (non-PA) and 0.0764 (PA) for $\lim_{q\to\infty} \Omega/(q^3k_BT/\eta_0)$ and 1.596 for R_G/R_H, respectively. Here PA is an abbreviation of the preaveraged Oseen tensor. A hypothetical pseudo-Gaussian distribution, represented by $\nu = {}^3/_5$ and $t = l = 2$, contains no information on short-range correlation and gives 0.0788 (non-PA) and 0.0710 (PA) for $\lim_{q\to\infty} \Omega/(q^3k_BT/\eta_0)$ and 1.860 for R_G/R_H, respectively. The former values were first calculated by Benmouna and Akcasu,[12] and the latter by Akcasu and Han.[14] A special case is the Θ state with Gaussian distribution of $\nu = {}^1/_2$ and $t = l = 2$. Partly mentioned already, this case gives 0.0625 (non-PA) and 0.0530 (PA) for $\lim_{q\to\infty} \Omega/(q^3k_BT/\eta_0)$ and 1.505 for R_G/R_H. The former values are equal to the results reported by Benmouna and Akcasu[12] and Akcasu and Gurol,[4] and the latter by Kirkwood.[5] The results for these three cases are summarized in Table I.

It is found from the table that in the swollen chain state, eq 11 and 14 give always larger values of $\lim_{q\to\infty} \Omega$ and R_G/R_H than those at $\nu = 0.5$ and $l = t = 2$. The calculated TK value $R_G/R_H = 1.596$ explains well the experimental value 1.50, which has very recently been reported by us for a rubbery polymer, polyisoprenes, in a good solvent (cyclohexane).[2] A value $R_G/R_H = 1.64$ has also been obtained recently by Barrett[15] by Monte Carlo experiments with parameters $l = t$ and $\nu = {}^3/_5$ in eq 4. The renormalization group (RG) calculation to order ϵ^2 by Wang et al.[16] has also predicted a similar value, 1.60, and that to order ϵ by Oono and Kohmoto[17] has given 1.51 for R_G/R_H of non-PA nondraining chains. The latter is in excellent agreement with the experimental result. However, some questions may be posed about this agreement if one considers the discrepancies between experiments and the RG results for R_G/R_H in the Θ state and $\lim_{q\to\infty} \Omega/(q^3k_BT/\eta_0)$ in good and Θ states, as described below. On the other hand, the calculated value $\lim_{q\to\infty} \Omega/(q^3k_BT/\eta_0) = 0.075\,38$ for highly swollen chain of TK distribution with non-PA is still far (20% *larger*) from the experimental one, 0.0616. This disagreement is due directly to the fact that eq 11 is independent of l and t and suggests that the short-range correlation between chain elements, which was treated in the scaling form, is still insufficient to describe Ω at the q^3 regime, where short element distances are much more important than at smaller q. In RG calculations to order ϵ, Oono[18] has given that $\lim_{q\to\infty} \Omega/(q^3k_BT/\eta_0) \approx 0.050$ for non-PA nondraining chains. This value is *smaller* (20%) than experimental one, 0.0616, and is in contrast to TK and pseudo-Gaussian results, which are both *larger* than 0.0616. Thus, it cannot be explained well why, as described in Introduction, the experimental Ω value is close to the Θ results, 0.0625, calculated for non-PA nondraining chains. In this connection, it may be interesting to note a study by Tanaka and Stockmayer,[19] who developed a first-order perturbation expression of Ω by the same scheme as in the present work and showed that, for non-PA chains, $\lim_{q\to\infty} \Omega/(q^3k_BT/\eta_0) = 0.0625$ independent of excluded volume. After all, we have the following suspicion that the discrepancies between experiments and theories for $\lim_{q\to\infty} \Omega/(q^3k_BT/\eta_0)$ could be due to (1) the insufficiency of the Oseen description for the hydrodynamic interaction in the Kirkwood formula and/or (2) the approximate nature (or a lack of accuracy) of the Kirkwood formula. Through the dynamical RG description of R_H to order ϵ^2, Wang et al.[20] have recently found that within Kirkwood–Riseman model, the strength of hydrodynamic interaction is decreased with an increase in the excluded volume interaction. According to this description, the hydrodynamic effects on chain dynamics are very small in good solvent and the term (2) becomes a main origin of the discrepancies. However, our recent experimental results[2] for a rubbery polymer in good solvent (polyisoprenes in cyclohexane) have never shown any draining nature in both R_H and Ω. Moreover, our successive works on polyisoprenes in the Θ state[21] have revealed that there are distinct discrepancies between experimental and theoretical results for both R_G/R_H and $\lim_{q\to\infty} \Omega/(q^3k_BT/\eta_0)$. As shown in Table I, the experimental results in the Θ state are that $R_G/R_H = 1.30$ and $\lim_{q\to\infty} \Omega/(q^3k_BT/\eta_0) = 0.048$, and both are clearly different (ca. 15% and 25%) from the Gaussian calculations 1.505 and 0.0625 (non-PA), respectively. For R_G/R_H, recent RG calculations have given 1.19,[16,17] and Monte Carlo simulations 1.285[22] or 1.24 ~ 1.30[23] for non-PA nondraining chains. The former is still 10% smaller than the experimental result, and the latter agrees with experiments. However, the latter agreement seems to be apparent because the Monte Carlo simulations yield the value of a completely rigid body motion.[24] For $\lim_{q\to\infty} \Omega/(q^3k_BT/\eta_0)$, the RG calculations for non-PA nondraining chains have given 0.027.[18] This value is not only far from but also *smaller* than the experimental result and is again in contrast to 0.0625 (non-PA) and 0.0530 (PA) by Benmouna and Akcasu,[12] which are *larger* than experimental value. The presence of ternary interactions may also cause the discrepancies in the Θ state. Further, it should be remarked that the eq 13 does not include the coupling between internal and translational motions of the polymer, and thus the calculated D yields the short-time (=time zero) diffusion coefficient, whereas the experimental D measures the long-time one. The distinction between them is due to the deformation in the chain element distribution during diffusion, although it was reported to be on the order of a few percent for non-PA nondraining chains.[24]

In conclusion, the situation mentioned above suggests to us that the discrepancies could not be attributed to only one of the terms (1) and (2). It seems to be relevant at present that the terms (1) and (2) are both responsible for the discrepancies between experiments and theories.

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Diffusion of Macromolecular Stars in Linear, Microgel, and Network Matrices

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ABSTRACT: Tracer diffusion coefficients for star-branched polystyrene diffusing into linear, intramolecularly cross-linked (microgel), and intermolecularly cross-linked (network) polystyrene matrices were measured by forward recoil spectrometry. The diffusion behavior can be modeled by assuming that constraint release and arm retraction mechanisms are both operating. Microgels and networks behave as if they are linear chains of infinite molecular weight, so that only the arm retraction contribution is measured. It is found that, for a given arm molecular weight, four- and eight-arm stars diffuse about as quickly as three-arm stars in microgel matrices. A simple arm retraction mechanism is proposed whereby diffusive steps occur each time a single arm retracts, giving rise to a relatively weak dependence of the diffusion coefficient on the number of arms of the star.

Introduction

Star-branched polymers are frequently used as model systems for studying the effects of branching on rheological properties. In the Doi–Edwards tube model,[1-3] stress relaxation occurs as molecules withdraw from the tube within which they were originally confined. For star molecules, this process requires the retraction of arms to the branch point. The time scale for arm retraction is predicted to depend exponentially on the length of the arms.[4] Viscoelastic properties are not expected to depend on the number, f, of arms joined at the branch point, since conformational adjustment can take place by the independent retraction of different arms. Experimental studies have confirmed this expectation.[5,6] The diffusion of stars in a network requires a net translation of the center of mass, so the situation here is somewhat different. Current theoretical treatments assume that the branch point is fixed by network constraints unless all but two of the arms retract simultaneously. An arm retraction contribution to the tracer diffusion coefficient is obtained which has the following form:[7,8]

$$D_{\mathrm{ar}} = D_0^{\mathrm{AR}} M_{\mathrm{a}}^{-\beta} e^{-\alpha(f-2)M_{\mathrm{a}}} \qquad (1)$$

Here α, β, and D_0^{AR} are model-dependent constants and M_{a} is the molecular weight per arm. Experimental evidence for the exponential M_{a} dependence for three-arm stars has been obtained.[9,10]

The constraints which define the Doi–Edwards tube in a linear polymer melt (as opposed to those of a network) are not necessarily fixed, so diffusion of a star macromolecule can take place by the motion of the tube itself. The relevant time scale for this constraint release mechanism is determined by the relaxation time, τ_{e} of the molecules defining the constraints. The relaxation time for linear molecules scales as the cube of the molecular weight, and most theories of constraint release give the following form for the diffusion coefficient:[8]

$$D_{\mathrm{cr}} = D_0^{\mathrm{CR}} M^{-1} P^{-3} \qquad (2)$$

Here M is the total molecular weight of the diffusing species, and P is the molecular weight of the matrix chains. If diffusion by arm retraction and by constraint release are independent processes, the total tracer diffusion coefficient for a star molecule in a matrix of linear chains will be given by the sum

$$D^* = D_{\mathrm{cr}} + D_{\mathrm{ar}} \qquad (3)$$

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