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Statistical Parameters for Hydrogen Bonding Networks: One Component Case*

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Based on the analysis of network structures formed by hydrogen bonds as the sol–gel phase transition takes place in a single component hydrogen bonding system, the theory of reversible gelation is applied to calculate some statistical parameters that determine many physical and chemical properties of the networks. Then, the numerical simulation of the number of active chains and dangling chains, the number of effective cross-linkages, the number of active and dangling mers and the modulus as a function of conversion are undertaken.

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Hydrogen bonding (HB) is a donor–acceptor interaction specifically involving hydrogen atoms. As an active field, hydrogen bonding is currently considered to be an important field and has attracted the intense attention of chemists, physicists, biologists and engineers. This is due to the fact that HB plays a key role in the descriptions of transfers of protons,[1] supercritical fluids,[2] supramolecular design,[3] polymer solutions,[4] crystal engineering and biological molecules, etc. So far, much research on properties of hydrogen bonds has been performed from both the experimental and theoretical interest, which include nuclear magnetic resonance (NMR) line shift measurements,[5] neutron and x-ray diffraction,[6] lattice-fluid theory,[7] molecular dynamics (MD) and Monte Carlo simulations, *ab initio* calculations,[8] and so on. Almost all of these works are focused on the properties of HB clusters and networks. Therefore, studying the properties of HB clusters and networks opens an important way of investigating the properties of HB systems.

For the HB systems containing a large number of clusters associated by hydrogen bonds, an appropriate statistical method should be desired to describe such a system. In a previous paper[9] we have proposed that the statistical theory of reversible gelation[10–12] can be used to study some properties of the HB system due to the astonishing similarities between the formation of hydrogen bonds and reversible polycondensation. Interestingly, HB clusters can form a macroscopic space-filling network (gel effect) under proper conditions, so evaluating the statistical structure parameters of the HB network and studying its physical and chemical properties become considerable interest and offer the possibility of investigating properties of HB liquid or solutions. This is the main content of this letter.

The present discussion is still performed for the single component R-A_aB_b system as that in the previous letter, i.e., the molecule R-A_aB_b possessing a functional groups of proton–donor, proton–acceptors B with the total coordination numbers b and a group R which does not form a hydrogen bond.

To make the discussion easier, some notations are introduced as follows: N is the total number of molecules R-A_aB_b, p_a (p_b) the equilibrium conversion of species A(B), $r(r=b/a)$ the stoichiometric ratio of the two species A and B, which leads to the relationship $p_a = rp_b$ because of the balance condition of functional groups A and B.

In such an HB system, molecules can connect one-by-one through hydrogen bonds and form HB chains and HB loops under proper conditions, and then with size-growing of chain and loop structures and cross-linking among them, a macroscopic cluster or the network forms; this is the threshold of the sol–gel phase transition process in the HB system. The appearance of the network means that conversions p_a and p_b satisfy $p_a \geqslant (p_a)_c$ and $p_b \geqslant (p_b)_c$, where $(p_a)_c = r\,(p_b)_c = \sqrt{r}\left[\sqrt{ab} + \sqrt{(a-1)\,(b-1)}\right]^{-1}$ is the gelation condition and also the critical points of the sol–gel phase transition of the R-A_aB_b system.

Once the sol–gel phase transition occurs in the system, the molecule R-A_aB_b could only exist in the following four ways: (1) it belongs to the sol as all its functional groups (proton–donors and proton–acceptors) link to a finite cluster; (2) it is called a dangling mer as only one of its functional groups links to a gel network; (3) it is called an effective elastic mer as only two of its functional groups link to a gel network; (4) it is called an effective cross-linkage as three or more of its functional groups link to a gel network. Now, let us analyse the network structure consisting of the chains and loops. It is known that the effective elastic mers connect and form an active chain which is closely related to the elasticity of the network, while dangling mers associate and form a dangling chain which is usually related to the relaxation and damping property of the network.[13] Inside the HB network, the chains include active chains and dangling chains, the loop structure includes elastic active loops and dangling loops. The dangling chains and loops have no contribution to the elasticity of the HB network, and their existence usually leads to overestimation in viscoelastic property of the network and viscosity of the system; hence they are called the defects of the network. Thus it is useful to calculate these network structural parameters for discussing the related properties of the HB system.[14]

Supposing that X and Y are the corresponding probabilities of finding that the proton–donor and

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proton–acceptor chosen at random link to the sol, by means of the reversible gelation theory, we can obtain

$$X = 1 - p_a + p_a x, \tag{1}$$

$$Y = 1 - p_b + p_b y, \tag{2}$$

where $x = SX^{-1}$, $y = SY^{-1}$ and $S = X^a Y^b$ are the expressions of the sol fraction. Naturally, the probabilities of finding the proton–donor and proton–acceptor linking to the gel network should be $1 - X$ and $1 - Y$, respectively. If one defines a quantity p_{ij} as

$$p_{ij} = \left[C_a^i (1-X)^i X^{a-i}\right]\left[C_b^j (1-Y)^j Y^{b-j}\right] \tag{3}$$

which denotes the probability of finding i proton–donors and j proton–acceptors of a molecule linking to gel simultaneously, then according to the analysis mentioned above, $n_{\rm s}$ (the number of molecules being in the sol), $n_{\rm e}$ and $n_{\rm d}$ (the number of effective elastic and dangling mers respectively), and $P_{\rm e}$ (the number of effective cross-linkages) can be expressed as

$$n_{\rm s} = N p_{00}, \tag{4}$$

$$n_{\rm e} = N\left(p_{02} + p_{20} + p_{11}\right), \tag{5}$$

$$n_{\rm d} = N\left(p_{01} + p_{10}\right), \tag{6}$$

$$\begin{aligned} P_{\rm e} &= N\Big[\Big(\sum_{i=3}^{a}\sum_{j=0}^{b} p_{ij} + \sum_{i=0}^{a}\sum_{j=3}^{b} p_{ij} - \sum_{i=3}^{a}\sum_{j=3}^{b} p_{ij}\Big) \\ &\quad + \left(p_{21} + p_{12} + p_{22}\right)\Big] \\ &= N\Big[1 - p_{00} - \left(p_{10} + p_{01}\right) - \left(p_{02} + p_{11} + p_{20}\right)\Big]. \end{aligned} \tag{7}$$

Note that Eq. (7) can be rewritten as $P_{\rm e} + n_{\rm s} + n_{\rm e} + n_{\rm d} = N$, this implies that the molecules indeed have four states mentioned above.

For the gel network, the chain segment between two cross-linkages is called the active chain, thus $N_{\rm e}$, the number of active chains, can be given by

$$\begin{aligned} N_{\rm e} &= N\Bigg[\sum_{i=2}^{a}\sum_{j=1}^{b}\frac{i+j}{2}p_{ij} + \sum_{i=1}^{a}\sum_{j=2}^{b}\frac{i+j}{2}p_{ij} \\ &\quad - \sum_{i=2}^{a}\sum_{j=2}^{b}\frac{i+j}{2}p_{ij}\Bigg], \end{aligned} \tag{8}$$

where the factor $(i+j)/2$ arises from the fact that two effective cross-linkages determine one elastic chain.

Now let us consider $N_{\rm d}$, the number of dangling chains in the system. If two or more functional groups of the R-$A_a B_b$ molecules link to the gel network, then the number of dangling chains associated with this molecule must equal that of the functional groups reacted and linked to a finite cluster. This leads to

$$\begin{aligned} N_{\rm d} = N[&\left(\sum_{i=2}^{a}\sum_{j=0}^{b} + \sum_{i=0}^{a}\sum_{j=2}^{b} - \sum_{i=2}^{a}\sum_{j=2}^{b}\right)\tilde{p}_{ij} \\ &\cdot (a - i + b - j) + (a + b - 2)\tilde{p}_{11}, \end{aligned} \tag{9}$$

where

$$\begin{aligned} \tilde{p}_{ij} = &C_a^i (1-X)^i \left[X - (1-p_a)\right]^{a-i} \\ &\cdot C_b^j (1-Y)^j \left[Y - (1-p_b)\right]^{b-j}. \end{aligned}$$

Through a direct calculation, we obtain

$$\begin{aligned} N_{\rm e} = &\frac{N}{2}\big[b(1-Y) + a(1-X) \\ &- 2\left(p_{20} + p_{02} + p_{11}\right) - \left(p_{10} + p_{01}\right)\big], \end{aligned} \tag{10}$$

$$\begin{aligned} N_{\rm d} = &N p_a^a p_b^b \{1 + a f_a(x) + b f_b(y) \\ &+ ab(a+b-2)(1-x)(1-y)x^{a-1}y^{b-1} \\ &- \left[1 - a f_{a-1}(x)\right]\left[1 - b f_{b-1}(y)\right]\}. \end{aligned} \tag{11}$$

In Eq. (11), the function $f_n(\alpha)$ is defined as $f_n(\alpha) = \alpha\left[1 - n\alpha^{n-1} + (n-1)\alpha^n\right]$.

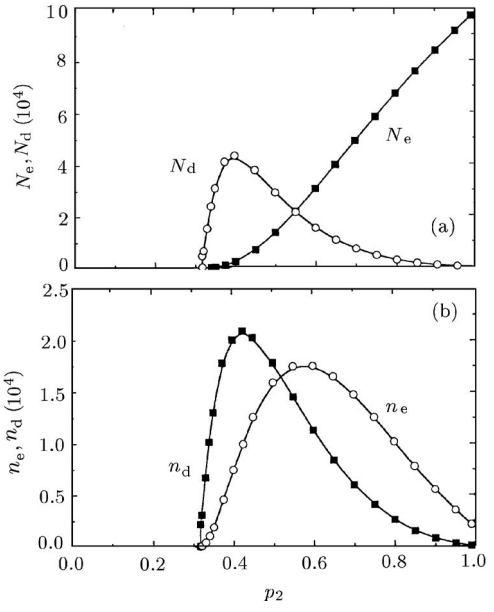

Fig. 1. Plots of $N_{\rm e}$, $N_{\rm d}$, $n_{\rm e}$ and $n_{\rm d}$ versus conversion p_2.

The modulus G of the network under the condition of neglecting the entanglements is[15]

$$\begin{aligned} G &= \frac{F k_{\rm B} T}{V}\left(N_{\rm e} - P_{\rm e}\right) \\ &= \frac{F k_{\rm B} T N}{2V}\left[(a+b-2) - (aX + bY) + n_{\rm d} + 2n_{\rm s}\right], \end{aligned} \tag{12}$$

where $k_{\rm B}$ denotes the Boltzmann constant, F is a constant, T the absolute temperature and V the volume of the HB system.

Moreover, the number fraction $f_{\rm en}$ and weight fraction $f_{\rm ew}$ of the effective chains defined by

$$f_{\rm en} = \frac{N_{\rm e}}{N_{\rm e} + N_{\rm d}}, \quad f_{\rm ew} = \frac{n_{\rm e}}{n_{\rm e} + n_{\rm d}} \tag{13}$$

can be obtained by substituting Eqs.(5), (6), (10) and (11) into Eq.(13).

From the above expressions for these statistical parameters, we can conclude that structural parameter values of these networks depend on the conversions p_a and p_b, which determine the probabilities X and Y. To show their variation with the conversions, we supply the numerical simulation for the R-A_aB_b system under the conditions of $N = 50000$, $a = 3$ and $b = 2$. Here, for brevity, only the plots of N_e, N_d, n_e, n_d, P_e and G varying with conversion are shown in Figs. 1 and 2.

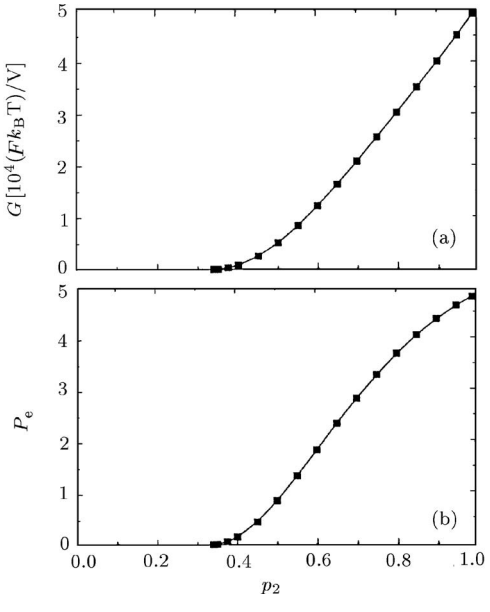

Fig. 2. Plots of G_e and P_e versus conversion p_2.

It can be seen from Figs. 1 and 2 that above the critical point of 0.317 for the present case, the effective cross-linkages, the number of active chains and the modulus all increase with the increasing conversion. This implies that the elastic property and viscosity of the HB system become greater. However, the number of dangling chains and the number of effective elastic and dangling mers have a tendency to increase and approach their maximum with the increasing conversion, and then decrease and approach zero. This indicates that all the molecules will become effective cross-linkages as the conversion approaches unity. In addition, it is evident that there exist maxima for quantities N_d, n_d and n_e in Fig.1. This is in essence due to the competition between intermolecular HB and intramolecular HB. Note that, after the gel point, the HB network has a loose structure with a large number of dangling chains and long active chains, and intermolecular HB is dominant. Therefore the number of dangling chains and dangling mers increase with the increasing of conversion. As the conversion becomes larger, intramolecular HB plays an important role and makes many dangling mers turn into effective elastic mers. Thus, the dangling chains and mers decrease and the corresponding maxima appear. As to the maximum of n_e in Fig. 1(b), it is obvious that n_e should have a tendency of increasing at a small conversion, but with the increasing conversion, the HB network is compact and more and more effective elastic mers form effective cross-linkages, which make n_e decrease.

In conclusion, we have calculated some statistical parameters of the HB network in a single component HB system. These parameters are useful to investigate the physical and chemical properties of the HB network and to provide the basis for further discussion on the HB system.

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