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The role of solvation on the conformational change during repeated freezing–thawing treatment to an extremely dilute aqueous solution of poly(vinyl alcohol)

Hu Yang[a,*], Rongshi Cheng[a,b,*], Hongfeng Xie[a], Zhiliu Wang[a]

[a]*Key Laboratory of Mesoscopic Chemistry of MOE and Department of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China*

[b]*College of Material Science and Engineering, Polymer Institute, South China University of Technology, Guangzhou 510640, People's Republic of China*

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Abstract

The effect of solvation–desolvation process on the conformational change of poly(vinyl alcohol) in an extremely dilute aqueous solution during the repeated freezing–thawing treatment was investigated by a differential refractometer. It was found that the hydrodynamic volume of PVA decreased regularly and smoothly with the number of freezing–thawing cycles treatment increasing, as the intra-molecular entanglement points made the polymer chain contract, and even in a full compacted globule state, there were still some solvent molecules in the chain. The extraordinary phenomenon was successfully explained and treated by a quantitative theory in terms of accompanying solvation–desolvation process during the macromolecular chain having contracted.

Keywords: Poly(vinyl alcohol); Solvation–desolvation effect; Cryogenic cycles treatment

1. Introduction

Solvation effect is an interesting and basic topic in polymer physical chemistry both in theory and experiments. It has been proved that solvated solvent molecules contact with polymer chain firmly and cannot be separated during size exclusion chromatographic process. In other words, the 'naked' polymer chain cannot be exists in the solution. There are a lot of experimental methods to detect the change of the solvation, especially in the mixture solvents, and the preferential adsorption coefficient is the most important parameter. But, it is difficult in a single solvent solution, as there is no different between the solvated and free solvent molecules. Cheng et al. [1–3] developed a special technique to study this problem from the change of the response constant of the differential refractive index detector before and after the separation in size exclusion chromatography. It is more attractive to study what will happen for the solvation effect during the conformation change of polymer chain, especially the coil-to-globule transition. Wu et al. [4,5] pointed out that there was still about 66% water inside the compacted globule even though poly(*N*-isopropylacrylamide) was in the thermodynamic globule state. This gives out a question where comes from so much solvent inside the globule. Cheng et al. [6,7] believed that there should be many network loops inside the globule during the coil-to-globule transition, and the trapped solvents cannot move freely which act as the solvated solvent based on the simple model.

It is well known that poly(vinyl alcohol) (PVA) aqueous solution will form gel if the cryogenic treatment is applied [8–10]. These phenomena result from the formation of the inter-molecular hydrogen bonds when the PVA chains come together. If decreasing the solution concentration to the threshold gelation concentration ($C<5\times10^{-5}$ g/ml), there will be only intra-molecular hydrogen bond during the freezing–thawing treatment, and the solution can be kept

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* Corresponding authors. Key Laboratory of Mesoscopic Chemistry of MOE and Department of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China. Tel.: +86 25 835 97355; fax: +86 25 833 17761.

E-mail addresses: yanghu@nju.edu.cn (H. Yang), rscheng@nju.edu.cn (R. Cheng).

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clear and can be studied by usual experimental methods [11–14]. Liu et al. [15,16] investigated the change of the viscosity property with the freezing–thawing cycles treatment to the PVA extremely aqueous solution, whose experimental result reveals that the hydrodynamic volume decreases with the freezing–thawing cycles, as the only intra-molecular hydrogen bond has formed.

In this paper, the solvation–desolvation process of the poly(vinyl alcohol) extremely dilute aqueous solution was investigated by a differential refractometer synchronously with the viscosity measurement mentioned above during the repeated freezing–thawing treatment. A quantitative theoretical equation to calculate the trapped solvent molecules by the network loops is deduced from the change of the refractive index increment. The equation is applied to the PVA aqueous solution, and the results have been discussed carefully.

2. Experimental

2.1. Material

Poly(vinyl alcohol) (PVA) sample used in this work was a commercial product. The degree of the polymerization (DP) is from 2400 to 2500, and the degree of saponification (DS) is from 98.0 to 99.0 mol%. The weight average molecular weight of the sample is 1.14×10^5 g/mol, determined by static light scattering.

2.2. Solution preparation

A known amount of PVA was dissolved in a small amount of de-ionized water, and refluxed for 2.5 h. The stock solution was diluted to 3×10^{-5} g/ml, and transferred into a flask. The flask was immersed into liquid nitrogen for 30 min, then taken out and thawed for 24 h at room temperature. This process was named as one cycle of freezing–thawing. In order to measure the change of the refractive index increment accurately, the treated solution was concentrated by evacuation at ambient temperature until it came to the desired concentration. Its exact concentration was determined by weighting the remaining polymer after evaporation of water.

2.3. Refractive index increment measurement

The refractive index increment was measured on a differential refractometer (model: DF-600). The instrument was calibrated by NaCl and KCl aqueous solution. The value of the constant (k), which is the relative constant between Δn and Δd ($\Delta n=k\times\Delta d$), was 8.014×10^{-4}. The refractive index increment of the PVA aqueous solutions with different thermo-history were all measured at 30 °C.

3. Theory

It is well known that the solvated solvent molecules contact with polymer chain firmly, and act as a part of the polymer. The observed solution properties are the summation of the ‘naked’ polymer chain and solvated solvent. So, the observed specific refractive index increment (S.R.I.I.) of polymer solution can be expressed as:

$$\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\mathrm{obs}} = w_{\mathrm{p}}\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\mathrm{p}} + w_{\mathrm{s}}\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\mathrm{s}} \tag{1}$$

here w_{p}, w_{s} are the weight fraction of the polymer and solvated solvent, and have $w_{\mathrm{s}}+w_{\mathrm{p}}=1$. $(\mathrm{d}n/\mathrm{d}c)_{\mathrm{p}}$, $(\mathrm{d}n/\mathrm{d}c)_{\mathrm{s}}$ are the refractive index increment of ‘naked’ polymer chain and the solvated solvent respectively. In a single solvent system, $(\mathrm{d}n/\mathrm{d}c)_{\mathrm{s}}=0$.

$$\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\mathrm{obs}} = (1-w_{\mathrm{s}})\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\mathrm{p}} \tag{2}$$

According to Eq. (2), the refractive index increment of the solvated polymer must be lower than that of the hypothetical ‘naked’ polymer. In other word, the refractive index increment of the polymer solution decreases with the degree of solvation increases. Eq. (2) can be rewritten as:

$$w_{\mathrm{s}} = \left[\frac{\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\mathrm{p}} - \left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\mathrm{obs}}}{\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\mathrm{p}}}\right] \tag{3}$$

If denoted the refractive index increment of the polymer chain in its maximum solvation state as:

$$\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\mathrm{F}} = \left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\mathrm{obs}}$$

and at this time

$$w_{\mathrm{s}} = \frac{nxM_{\mathrm{s}}}{nxM_{\mathrm{s}} + xM_0} \tag{4}$$

here x is the degree of polymerization; M_{o}, M_{S} are the molar mass of the repeat unit and solvent respectively; n is the number of solvated solvent molecules per monomer.

According to Eqs. (3) and (4), it can be reached:

$$n = \left[\frac{M_0}{M_{\mathrm{s}}}\right]\left[\frac{\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\mathrm{p}} - \left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\mathrm{F}}}{\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\mathrm{F}}}\right] \tag{5}$$

From Eq. (5), the $(\mathrm{d}n/\mathrm{d}c)_{\mathrm{p}}$ or n can be calculated.

The previous work has already demonstrated that there will form physical entanglement points during the polymer chain contraction. This entanglement is stable enough at room temperature, and the polymer conformation depends on its thermo-history [17–19]. It can be imagined that it should lost at least two solvated solvent molecules if one physical entanglement point is generated. At the same time, it forms a new polymer chain loop. There are two effects should be considered: first, the lost of the solvated solvent induces the increasing the refractive index increment according to Eq. (2); secondly, the chain loop may trap some non-solvated solvent molecules which act as same as the solvated solvent. This causes the decreasing the refractive index increment in the same reason. At this point, the weight fraction of the solvated solvent should be re-written as:

$$w_s = \frac{nxM_s + N(N)M_s}{xM_0 + nxM_s + N(N)M_s} \tag{6}$$

here $N(N)$ is the net increasing number of the 'solvated' solvent molecules per polymer chain on account of the trapping effect.

Then, we can reach:

$$\left(\frac{dn}{dc}\right)_{obs} = \frac{xM_0}{x(M_0 + nM_s) + N(N)M_s}\left(\frac{dn}{dc}\right)_p \tag{7}$$

Furthermore, if we consider the net increasing 'solvated' solvent per repeat unit, the above equation can be rearranged as:

$$\frac{N(N)}{x} = \left[\frac{\left(\frac{dn}{dc}\right)_p}{\left(\frac{dn}{dc}\right)_{obs}} - 1\right]\frac{M_0}{M_s} - n \tag{8}$$

According to Eq. (5):

$$\left(\frac{dn}{dc}\right)_p = \left(\frac{nM_s}{M_0} + 1\right)\left(\frac{dn}{dc}\right)_F \tag{9}$$

Finally, Eq. (8) can be expressed according to the experimental determined parameters as:

$$\frac{N(N)}{x} = \left[\frac{\left(\frac{dn}{dc}\right)_F}{\left(\frac{dn}{dc}\right)_{obs}} - 1\right]\left(\frac{M_0}{M_s} + n\right) \tag{10}$$

If there is the intra-molecular cohesional entanglement point m and N_0 solvent molecules are trapped by each loop, it has

$$N(N) = mN_0 \tag{11}$$

It is another interesting parameter that how much solvent molecules are trapped by each loop. This can be treated following the change of the polymer chain from coil to globule. The expansion factor g and g' can be defined as usual:

$$g = \frac{\langle S^2\rangle}{\langle S^2\rangle_0} \tag{12}$$

and:

$$g' = \frac{[\eta]}{[\eta]_0} \tag{13}$$

here $\langle S^2\rangle$, $\langle S^2\rangle_0$ and $[\eta]$, $[\eta]_0$ are the mean-square gyration radius and intrinsic viscosity at the experimental condition and the θ temperature, respectively. These two parameters have the theoretical relationship:

$$g' = g^{\omega} \tag{14}$$

and ω may take the value 1.5, 1 or 0.5 [20–22].

The expansion parameter g' is related to the intra-molecular cohesional entanglement points directly according to Edwards et al. [23] proposed:

$$g' = \frac{1}{(1+m)} \tag{15}$$

here, m is the number of the intra-molecular cohesional entanglement points. The above theoretical equation can be modified further to fit the experimental results [24,25].

$$g' = \frac{1}{(1+m)^Q} \tag{16}$$

Q is the empirical constant.

From the point of the change of the refractive index increment during the change of the polymer conformation, a new parameter can be defined similarly:

$$g_V = \frac{\left(\frac{dn}{dc}\right)_{obs}}{\left(\frac{dn}{dc}\right)_F} \tag{17}$$

Combined the Eqs. (6) and (7), the parameter g_V can be expressed as follow:

$$g_V = \frac{1}{\left[1 + m\frac{N_0}{x}\frac{M_s}{(nM_s+M_0)}\right]} \tag{18}$$

Compared the Eqs. (16) and (18), it comes:

$$g_V^{1/Q} = g' \tag{19}$$

If defined χ as:

$$\chi = \frac{g_V}{g'^{1/Q}}\left[\frac{1 - g'^{1/Q}}{1 - g_V}\right] \tag{20}$$

Inserting Eqs. (18) and (19) into Eq. (20) and rearranged:

$$\chi = \frac{(nM_s + M_0)x}{M_sN_0} \tag{21}$$

Finally, the number of the entrapped solvent molecules in each loop can be deduced as follow:

$$N_0 = \frac{x}{\chi}\left(n + \frac{M_0}{M_s}\right) \tag{22}$$

4. Results and discussion

The poly(vinyl alcohol) aqueous solution can form physical gel if the solution undergoes the cryogenic treatment. This phenomenon comes from the inter-and intra-molecular entanglement (hydrogen bond interaction) during the contraction of the polymer chain. It was reported that there would be only intra-molecular entanglement when the concentration was lower than the threshold gelation value [11–14]. This type of the entanglement is stable

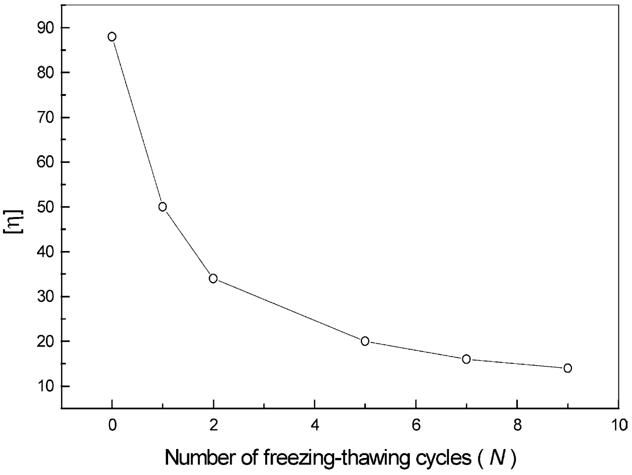

Fig. 1. The intrinsic viscosity of PVA aqueous solution as a function of the number of freezing–thawing cycles treatment (*N*) [15,16].

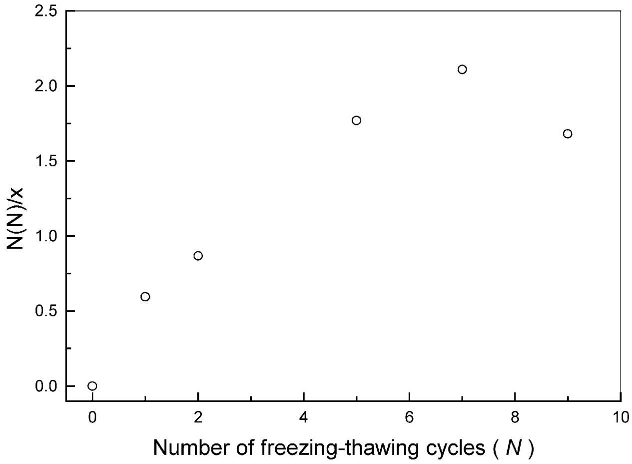

Fig. 3. The number of the 'trapped solvated' solvent molecules per repeat units as a function of the number of freezing–thawing cycles treatment (*N*).

Table 1
The data of intrinsic viscosity [η], $(dn/dc)_{obs}$, the net increasing 'solvated' solvent per repeat unit $(N(N))/(x)$, the extended factor g', g_V the solvent molecules number trapped by per loop N_0 and the number of the entanglement point (m), with the number of the freezing–thawing cycles treatment

N_{cyc}	[η]	$(dn/dc)_{obs}$	$(N(N))/(x)$	g'	g_V	N_0	m
0	88	0.156	0	1	1	0	0
1	50	0.133	0.59	0.568	0.853	698	6
2	34	0.124	0.87	0.386	0.799	230	29
5	20	0.103	1.77	0.227	0.661	69	198
7	16	0.097	2.11	0.182	0.622	37	438
9	14	0.105	1.68	0.159	0.672	18	710

enough at room temperature and can be enhanced with the repeated freezing–thawing treatment. Fig. 1 is the plot of the intrinsic viscosity with the number of the freezing–thawing cycles of the PVA aqueous solution as reported by Liu et al. [15,16]. This experimental result reveals that the hydrodynamic volume decreases with the number of freezing–thawing cycles, as the entanglement points make the polymer chain contract. The refractive index increment varies with the number of the freezing–thawing cycles have been also measured. However, since the concentration of PVA undergone the repeated freezing–thawing treatment is at about 3×10^{-5} g/ml, which is too low to measure the refractive index increment by differential refractometer correctly, the treated solution is concentrated by evaporation of solvent at ambient temperature until it comes to the desired concentration, then the refractive index increment is measured as showed in Fig. 2, and its exact concentration is determined by weighting the remaining polymer after evaporation of water. Similarly, the refractive index increment decreases with the freezing–thawing cycles within 7 cycles. Afterwards, it will increase slightly. As the concentration of PVA undergone cryogenic treatment is extremely low as mentioned above, only the intra-molecular entanglement can be formed. During this process, part of the solvated solvent molecules will disconnected from the polymer chain. At the same time, the new formed loop will trap some free solvent molecules which act as the 'solvated' molecules. If the later effect is larger than the former, the net effect will make the refractive index increment decrease as discussed in Eq. (7). The net increasing 'solvated' solvent molecules will arrive the maximum at $N=7$. As the number of freezing–thawing cycles treatment increases further, the size of the loop will decrease further, the total 'solvated' solvent will decrease contrarily. The reason is that the parts of 'solvated' solvent molecules are 'extruded' out of the loop even though the loop numbers still increase.

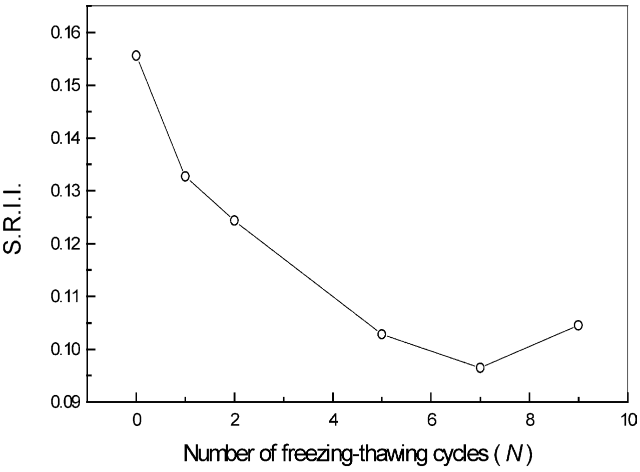

Fig. 2. The S.R.I.I. of PVA aqueous solution as a function of the number of freezing–thawing cycles treatment (*N*).

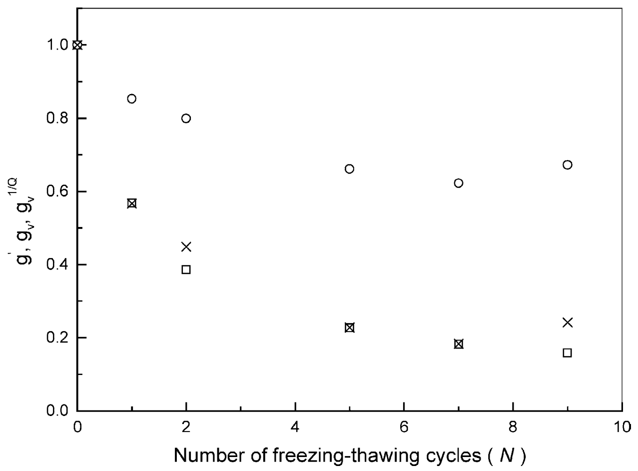

Fig. 4. The g', g_V and $g_V^{1/Q}$ ($Q=0.28$) of PVA aqueous solution as a function of the number of freezing–thawing cycles treatment (N). □, ○ and × are g', g_V and $g_V^{1/Q}$, respectively.

According to Eq. (10), the number of the 'trapped solvated' solvent molecules can be discussed quantitatively. If the state of PVA well dissolved in water was defined as the random coil without any entanglement point, it could be written as:

$$N = 0, \quad \text{and} \quad \frac{N(N)}{x} \to 0$$

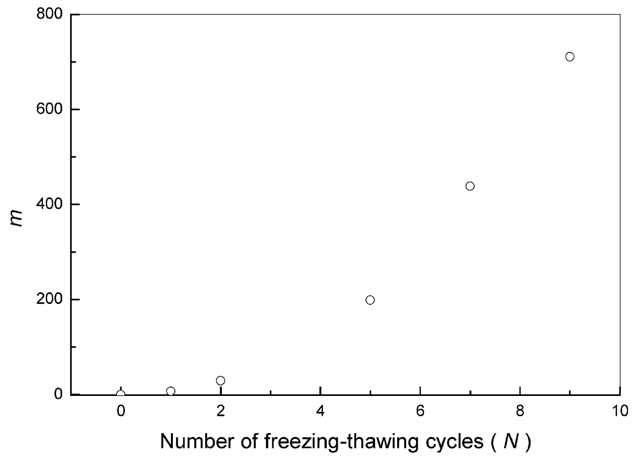

Fig. 5. The number of the entanglement point (m) within a PVA chain as a function of the number of freezing–thawing cycles treatment (N).

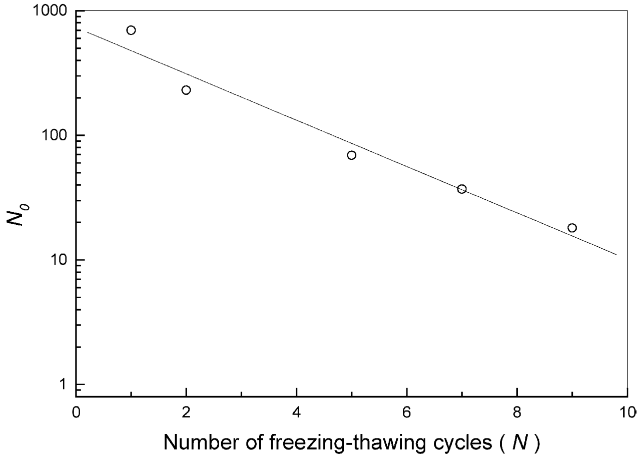

Fig. 6. The number of the trapped solvent molecules per loop (N_0) as a function of the number of freezing–thawing cycles treatment (N).

The number of the 'trapped solvated' solvent molecules per repeat units will come to the maximum value 2.1 when $N=7$ as listed in Table 1 and plotted in Fig. 3, and the number of solvated solvent molecules per monomer (n) is supposed 1. The parameters g', g_V and N_0 can be calculated according to the Eqs. (13), (17) and (22) respectively, and the results are listed also in Table 1. The experience parameter Q can deduced from the experimental data by the least-square fitting and equal to 0.28. The relationship between the parameters g', g_V, $g_V^{1/Q}$ and the number of freezing–thawing cycles are shown in Fig. 4. Actually, the parameters g' and g_V have the same physical means even though they are defined in different way. The expansion factor decreases with the number of freezing–thawing cycles as the intrinsic viscosity does.

The number of the entanglement point within a PVA chain can be calculated also from Eq. (16) and plotted in Fig. 5. It increases with the freezing–thawing cycles, or the decreasing of the expansion factor. As the length of each polymer chain is fixed, the size of the loop must shrink with the increasing of the entanglement point. Fig. 6 is the plot of the number of the 'trapped solvated' solvent per loop with the number of freezing–thawing cycles. Obviously, there are still some solvent molecules 'trapped' by the loops even the size of the loop is very small.

5. Conclusion

Based on the experimental data of the viscosity and refractive index increment of poly(vinyl alcohol) aqueous solution, the solvation–desolvation and 'trapped solvated' solvent molecules are discussed quantitatively. It proves that the decreasing of hydrodynamic volume results from the generated intra-molecular entanglement points during the polymer chain contract. At the same time, one entanglement point will form at least one loop. The loops may trap free solvent molecules which act as the 'solvated' solvent. This effect causes the value of refractive index increment decreasing further.

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