Characterization of the Conformational Changes of Partially Hydrolyzed Polyacrylamide Chains in Solution using Stress Recovery Experiment

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ABSTRACT: In this study, a simple empirical decay function model is fitted to the experimental data to characterize the conformational changes of partially hydrolyzed polyacrylamide (HPAM) in semidilute solutions, using the stress recovery experiment after cessation of a steady shear flow processing. With the increase of HPAM concentration and NaCl concentration, the parameter κ decreases, and this is in excellent agreement with the conformational changes of HPAM molecule chains. Experimental results show that the parameter κ can provide some information on the changes of the polymer chain conformation. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2709–2713, 2006

Key words: polymer solutions; stress recovery; conformational change

INTRODUCTION

Conformational properties of the polymer chains in solutions depend on both the solvent and the polymer concentration.[1] In a good solvent, where the energy of interaction between a polymer element and a solvent molecule adjacent to it exceeds the mean of the energies of interaction between the polymer–polymer and solvent–solvent pairs, the polymer chains will tend to expend further so as so reduce the frequency of contract between pairs of polymer elements. In a poor solvent, on the other hand, where the energy of interaction is unfavorable, a compact and rather stiff globule state in which polymer–polymer contracts occurs more frequently will be favored.[2] Meanwhile, effects of the concentration on conformational changes of polymer chains in solutions are also significant. Generally, the polymer solutions have the existence of three concentration regimes, for example, dilute, semidilute, and concentrated.[3,4] In the dilute regimes, it has been assumed that each molecule is far away from the others; the intermolecular interactions can be ignored. In this case, the molecules behave as individual units. The intermolecular interactions progressively become predominant as the concentration increases, and at a certain concentration C^* polymer molecules begin to overlap and eventually entanglement may develop.[5] Above this concentration, the solution is considered to be semidilute. Graessley[1] defined concentration C^{++} as given below

$$C^{++} = C^*[R^2(0)/R_\theta^2]^4 \qquad (1)$$

where $R^2(0)$ is the mean-square end to end distance at zero concentration; the subscript θ indicates theta conditions. At concentration $C > C^{++}$, the solution is considered to be concentrated (or melt).

In view of the above, the conformation of polymer chains will change at various conditions. Although various techniques were used to study conformational changes of polymer in solutions, such as the light-scattering, the small angle X-ray scattering (SAXS),[6] and the small-angle neutron scattering (SANS),[6,7] they require special equipment. In this paper, we developed a simple method of the stress recovery experiments to study the conformational changes of polymer chains in the semidilute regimes, without any complicated and special equipment. Interesting conclusions can be drawn from the experimental results regarding the conformational changes of the polymer chains in solutions.

EXPERIMENTAL

Materials

Partially hydrolyzed polyacrylamide (HPAM) was a commercial product of Pfizer, USA, and its molecular

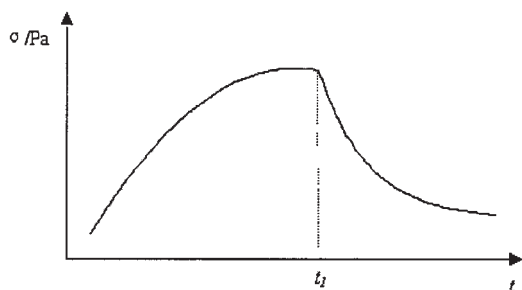*Correspondence to:* F. Zhao (zhf19752003@yahoo.com.cn).

Figure 1 Schematic representation in the shear stress creep/recovery experiment.

weight is stated to be $(15–17) \times 10^6$ g/mol with the degree of hydrolysis 26–28%, Sodium chloride (NaCl) was of analytical reagent grade (Beijing Xi Zhong Chemical Factory). All water used was doubly distilled.

Static light scattering

In static LLS, the z-average radius of gyration $\langle R_g^2 \rangle z^{1/2}$ (or written as $\langle R_g \rangle$) of the polymer chains from the angular dependence of the excess absolute scattering intensity is known as the Rayleigh ratio $R_{vv}(q)$, on the basis of

$$\frac{KC}{R_{vv}(q)} = \frac{1}{M_W}\left(1 + \frac{1}{3}\langle R_g^2\rangle q^2\right) + 2A_2C \qquad (2)$$

where $K = 4\pi n^2 (dn/dC)^2/N_A\lambda_0^4$ and $q = (4\pi n/\lambda_0)$ $\sin(\theta/2)$, with n, dn/dC, λ_0, and θ being the solvent refractive index, the specific refractive index increment, the wave length of the light *in vacuo*, and the scattering angle, respectively. For HPAM in aqueous solutions at 25°C, $[dn/dC]_{532.8 \text{ nm}} = 0.175$ mL/g.[8]

The stress creep/recovery experiment

The shear stress recovery measuring system used here is described in detail elsewhere.[9]

In this experiment, a constant low shear rate was applied at $t = 0$, we could observe the shear stress creep behavior and the shear stress increase smoothly to its stationary value, and then the imposed shear rate was suddenly removed and the recovery, on the release of the shear stress, was monitored, as shown in Figure 1. When $t > t_1$, the shear stress recovery behavior can be characterized by the following equations:

$$\sigma(t) = (\sigma_{max} - \sigma_{min}) \exp - (t/\tau)^\beta + \sigma_{min} \qquad (3)$$

$$\tau \propto \eta\kappa \qquad (4)$$

Originally, this function is a representation of dielectric relaxation,[10,11] here our experiment data can be described very well by eq. (3): where t is the experimental time; σ_{max} is the stationary shear stress at $t = t_1$; σ_{min} is final stress recorded at $t = t_f$; τ is the characteristic recovery time; η is viscosity of the polymer solutions; and κ is the conformational parameter (see results and discussion).

To analyze experimental data directly, eq. (3) was rearranged to obtain eq. (5)[12,13];

$$\ln \ln(1/R_{(t)}) = \beta \ln(t/\tau) \qquad (5)$$

where $R_{(t)}$ is equal to $(\sigma(t) - \sigma_{min})/(\sigma_{max} - \sigma_{min})$, and so eq. (5) follows a straight line with slope equal to β and intercept equal to $-\beta \ln \tau$. The values of τ can be calculated by fitting eq. (4) to the experimental data. If the viscosity η is known, the parameter κ in eq. (4) is calculated.

The determination of the concentration regimes

The intrinsic viscosity $[\eta]$ of HPAM in water was measured at room temperature by Ubbeldohe capillary viscometer (water flow time $\sim$ 136 s). Viscometric data were converted to reduced specific viscosity (η_{sp}/c), where c is the HPAM concentration and η_{sp} is defined by

$$\eta_{sp} = \frac{(\eta - \eta_0)}{\eta_0} \qquad (6)$$

Here η and η_0 are the viscosities of solution (HPAM/water) and solvent (water), respectively. Extrapolating
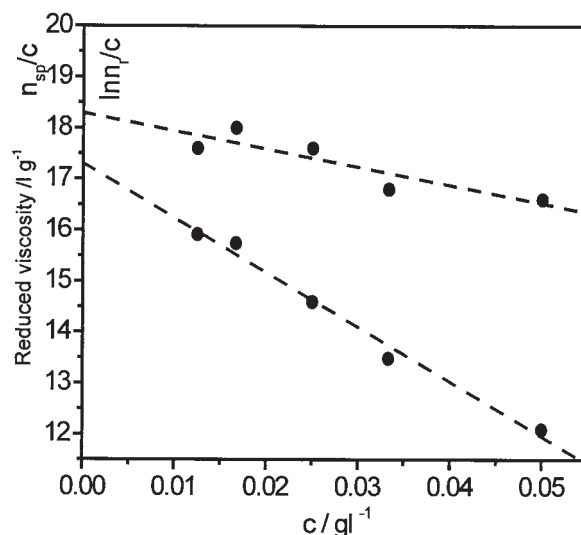

Figure 2 Reduced viscosity as a function of HPAM concentration, the broken lines represent the best fits to the experimental data.
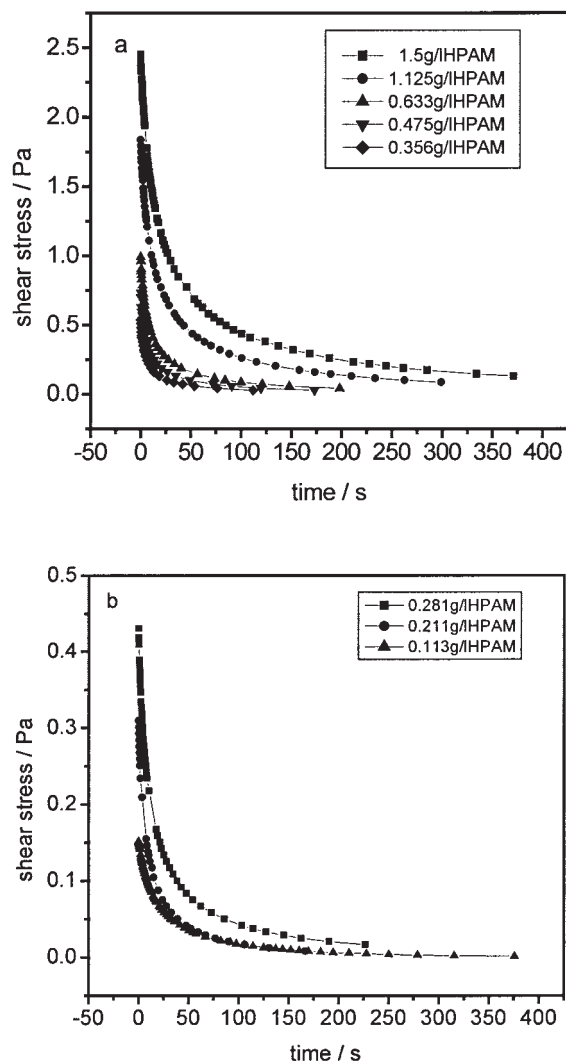
Figure 3 Plots of the shear stress recovery curve for HPAM solution, at various concentrations.

η_{sp}/c to zero polymer concentration gives the intrinsic viscosity $[\eta]$. A number of theoretical model for the determination of C^* have been presented.[14] A common feature of these models is that C^* varies as $[\eta]^{-1}$, for example,[15–17]

$$C^* = 1/[\eta] \qquad (7)$$

The overlap concentration C^* is not precisely defined, but it should correspond roughly to the concentration. In our experiments, reduced viscosity as a function of HPAM concentration is shown in Figure 2. From the Figure 2, one can see that reduced and relative viscosities do not coincide at zero concentration nicely, so that their average values are obtained. The intrinsic viscosity $[\eta]$ of HPAM in water is about 17.80 L/g, and then the overlap concentration C^* of the HPAM solution can be evaluated to be about 0.056 g/L by eq. (7). The HPAM solution concentration investigated in our
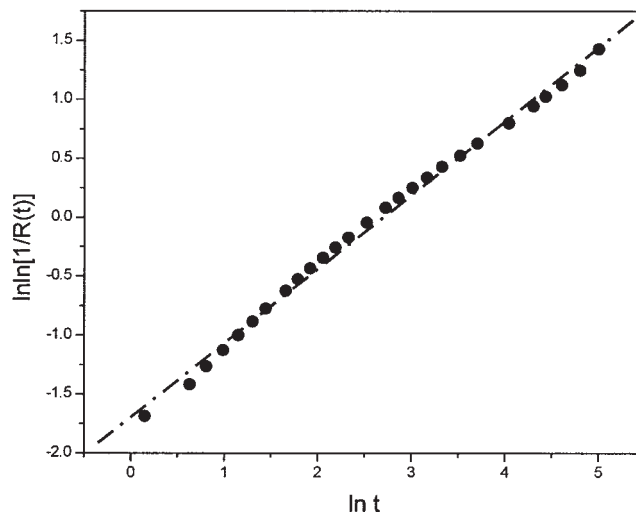

Figure 4 Double logarithmic plot of the recovery function ln ln$[1/R_{([infi]t)}]$ versus ln t for HPAM solution at $c = 633$ mg/L.

experiments is in the range of 0.1–1.5 g/L, which ensures that the concentration is in the semidilute regimes.

RESULTS AND DISCUSSION

Figure 3 represents plots of stress recovery curve for HPAM solution at various concentrations at the shear rate $\bar{\gamma} = 0.36$ s^{-1}. Figure 4 is a plot of the recovery function ln ln$[1/R_{(t)}]$ versus ln t for HPAM solution at $c = 633$ mg/L. The calculated average recovery time is obtained the with slope equal to β and intercept equal to $-\beta$ ln τ. The viscosities of polymer solutions at differential concentrations are measured using this cone-and-plate measurement system at $\bar{\gamma} = 0.36$ s^{-1}, and so corresponding values of κ is calculated by eq. (4). Values of κ at other concentrations are obtained through the same methods, too. Table I lists the data and the calculated results for various HPAM concentrations.

TABLE I
The Data and Calculated Results for the Various HPAM Concentrations

C_{HPAM} (g/L)	Viscosity (η, Pa s)	Recovery time (τ, s)	$\kappa \, \alpha \, \tau/\eta$ (Pa^{-1})
1.5	1.729	32.46	18.77
1.125	1.282	25.39	19.81
0.633	0.6937	14.86	21.36
0.475	0.5137	11.37	22.13
0.356	0.3865	8.35	21.62
0.281	0.3033	6.87	22.65
0.211	0.2173	4.95	22.78
0.113	0.1060	2.44	23.02

Figure 5 The curve of κ as a function of HPAM concentration.

TABLE II
The Data and Calculated Results at the Various NaCl Concentrations for HPAM Solution ($c = 1.5$ g/L)

C_{NaCl} (g/L)	Viscosity (η, Pa s)	Recovery time (τ, s)	$\kappa \propto \tau/\eta$ (Pa^{-1})
0.65	0.4274	23.4	54.76
0.85	0.3415	17.0	49.78
1.08	0.2898	14.2	49.00
1.43	0.2188	9.29	42.46
1.90	0.1775	7.04	39.67
2.24	0.1568	5.63	35.91
2.94	0.1337	4.33	32.38

Figure 5 shows the variation of κ as a function of HPAM concentration. The parameter κ decreases with the increase of HPAM concentration.

Figure 6 represents plots of stress recovery curve for HPAM solution($c = 1.5$ g/L) for various NaCl concentrations at the shear rate $\bar{\gamma} = 0.36$ s^{-1}. According to the aforementioned method, one can obtain the data and the calculated results for HPAM solution, at various NaCl concentrations, which is shown in Table II.

Figure 7 shows the calculated parameter κ as a function of NaCl concentration. With the increase of NaCl concentration, the parameter κ decreases. Now from the Figures 5 and 7, we may argue that the parameter κ is relative to the conformational changes of the polymer chains. In semidilute regimes, with increasing concentration, the excluded volume repulsion between segments in the same chain becomes screened by segments of the neighboring chains, and the polymer molecule's conformations change continuously. It is clear that the radius of gyration of the

molecule will decrease[6,18–20] so that the polymer conformation contracts progressively. In addition, as we know, HPAM is an anionic polyelectrolyte; the molecule chains will be extending due to the electrostatic repulsion between the charger monomers along HPAM chains. However, with the addition of NaCl, the HPAM molecules huddle up because of the screening of electrostatic repulsion along the chains, so that the polymer conformation also contracts with the increase of NaCl in solution.[21]

Here, we use the parameter κ to characterize the conformational changes of the polymer chains through rheological experiments. To demonstrate our conclusions further, we measure the conformational changes of the HPAM chains directly with the static light scattering. The radius of gyration of HPAM with the increase of concentrations is listed in Table III. It clearly shows the decrease in the radius of gyration of HPAM as the HPAM concentration increases, which agrees well with the changes in parameter κ.

From the above discussion, the polymer molecule conformational changes are in excellent agreement with that of the parameter κ and account quite well for our observation. It may, therefore, be reasonable to predict that the parameter κ can provide information on the change of the polymer configuration in solu-
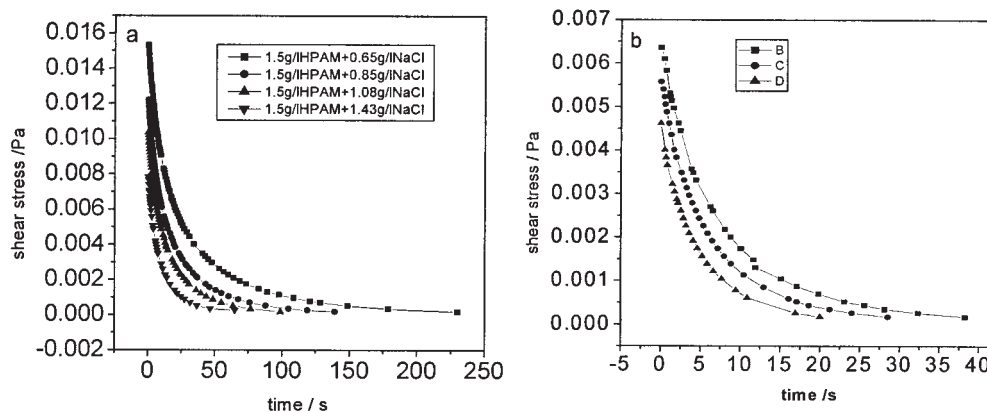

Figure 6 Plots of the shear stress recovery curve for HPAM solution ($c = 1.5$ g/L) at various NaCl concentrations.

tion. Theoretically speaking, in unperturbed condition, the polymer molecule conformation is in equilibrium with random coil; the molecules are more or less stretched and rotated around their gravity. When the external stimulus is given to the solution, the equilibrium state is broken, and the polymer molecule conformation will change with time. On the other hand, the polymer molecule conformation again returns to the equilibrium state after cessation of the external stimulus. During the process, a slower time relaxation can be observed due to the properties of the polymer macromolecule. The higher the polymer viscosity is, the longer the relaxation time is, and the bigger the polymer molecule conformation is, the longer the relaxation time is, too, so that we may obtain $\tau \propto \eta\kappa$, as expressed by eq. (4). Certainly, eq. (4) is only a empirical model equation, the strict mathematical relations among these parameters are difficult to estimate, at least from our experimental results reported in this paper, the values of κ calculated from our experiment are only relative, not absolute. However, it is certain that the conformational changes of the polymer chains in solution is described from the change in the tendency of κ, and it is a measurement of mean average size of polymer molecular chains.

CONCLUSIONS

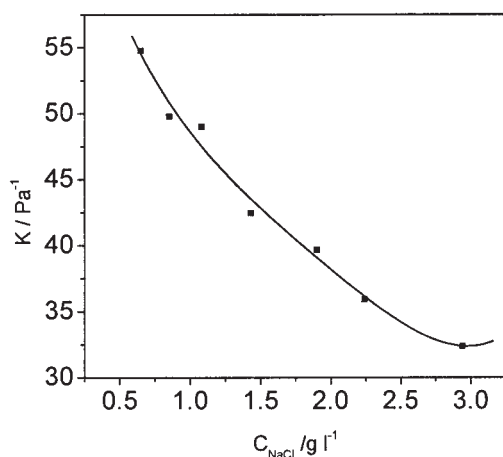In this paper, we characterize the changes of HPAM polymer chains with the parameter κ through the

Figure 7 The curve of parameter κ as a function of NaCl concentration at HPAM solution concentration $c = 1.5$ g/L.

TABLE III
Summary of LLS Results of Partially Hydrolyzed Polyacrylamide Vis Concentrations at 25°C

C_{HPAM} (10^4 g/L)	$<R_g>$ (nm)
1.05	98
1.50	107
2.0	110
2.3	116

shear stress recovery experiment. Results show that the parameter κ can provide information on the conformational changes of the polymer chains in solution. It is the measurement of mean average size of the polymer molecular chains.

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