

Universal Concentration Scaling on Rheometric Properties of Polydisperse and High Molecular Weight Polyacrylamide Aqueous Solutions

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Abstract A great progress has been made over the last decades in studying concentration scaling on rheometric properties of monodisperse polymer solutions. However, the effects of polydisperse polymer solutions on such a concentration scaling remain elusive. In this work, rheometric properties of industrially relevant polydisperse and high molecular weight polyacrylamide (PAAm) aqueous solution have been studied. The results show a concentration scaling of the characteristic relaxation time, the plateau modulus and the zero-shear viscosity across a concentration range from 10c* to 250c*. The time-concentration superposition principle is validated and extended in the data analysis of the terminal dynamic regime. The concentration scaling exponent of their shifting factors is significantly smaller than the results of monodisperse polymer solutions in good and θ solvents reported in the literature. The steady shear viscosity and shear stress of 18M PAAm aqueous solutions with relatively lower concentration ($\leq 35c^*$) could also be superimposed into a master curve with the shear-thinning exponent of 0.73 ± 0.03 and 0.27 ± 0.03 , respectively, over a wide range of shear rates in about six orders of magnitudes. However, for 18M PAAm aqueous solutions with higher concentration ($\geq 48c^*$) in an intermediate shear thinning regime, the scaling exponent shows a pronounced concentration dependence. The shear thinning exponent of steady shear viscosity varies from 0.73 to 0.57 as concentration is increased, and then increases from 0.57 to 0.90 from sufficiently high shear rate. Further increasing shear rate, the shear-thinning exponent of 18M PAAm aqueous solutions at all concentrations converges to the lower bounded value observed in the relatively less concentrated ($\leq 35c^*$) 18M PAAm aqueous solutions, i.e., 0.73 ± 0.02 for shear viscosity and 0.27 ± 0.02 for steady shear stress, respectively. It reveals that the concentration effects of polydisperse polymer solutions could be greatly reduced by the dynamic “molecular individualism” in strong shear flow.

Keywords Polymer solution; Polydispersity; Rheometric properties; Time-concentration superposition principle

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INTRODUCTION

Dynamic instabilities and highly nonlinear flow effects of complex fluids, such as turbulence drag reduction, elastic turbulence, extrudate distortion, shear banding,^[1–4] etc., are often encountered in many industrial applications such as long distance transportation of crude oil, intensive oil recovery, inkjet printing, spraying and extrusion. The origins of the nonlinear effects are rooted in the dynamic coupling of individual relaxation mode of complex fluids across a wide range of time and length scales. It has been well-established that the equilibrium or quasi-equilibrium properties of monodisperse flexible chain polymer solutions exhibit universal behaviour and under an isobaric condition can be defined by two thermodynamic state variables, namely polymer concentration and solvent quality,^[5] which is a measure of the interaction between the chain segments. The rheometric properties of

synthetic polymer and DNA solutions show concentration dependence.^[6–9] These data can be superimposed and drawn into a master curve, showing universal characteristics. In the concentration region of dilute solution, the longest characteristic relaxation time does not increase significantly with the increase of concentration. After the critical overlap concentration is exceeded, different power law exponents are shown in the semi-dilute unentangled and semi-dilute entangled concentration regions, and affected by the solvent quality. The results are consistent with the prediction of the dynamic scaling theory of polymer solutions.^[5]

The linear and nonlinear rheometric properties of polymer solutions result from their conformational evolution under local flow conditions. Under simple shear flow, molecular fluorescence microscopy techniques reveal that the conformation of molecular chains undergoes cycles of stretching-orientating-retracting-rolling.^[10] Their degrees of stretch and orientation fluctuate greatly, so that the chains could not achieve a stable stretched conformation. Different from the simple shear flow, the extensional flow is more efficient in the stretching of chain molecules. As the extensional rate ex-

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ceeds a certain critical value, the chain molecule would instantaneously change from the "random coil" to the "stretched" conformation, reaching a steady state. The corresponding extensional viscosity can be several orders of magnitude higher than the shear viscosity, showing strong viscoelasticity. Chain molecules undergo various conformations such as random coils, dumbbells, hairpins, knots, etc., showing significant "molecular individualism".^[11] The critical extensional rate required for the conformational transition from random coil to stretched state in a semi-dilute solution is larger than that of a dilute solution. The conformational distribution under the same extensional rate is also wider. The stretching effect of the extensional flow to the chain molecules in semi-dilute unentangled polymer solution is not as effective as that in dilute solution. Such a difference decreases with the increase of extensional rate. A universal curve of the average chain molecular extension with extensional rate could be obtained by rescaling the steady state conformation data of dilute and semi-dilute solution with the critical extensional rate. It shows that in high extensional rate flow, the chain molecules in a semi-dilute solution experience a flow environment like in a dilute solution. The influence of concentration tends to be small, indicating that the hydrodynamic interaction is the key factor that drives the dynamic evolution of polymer conformation and its dependence on *Weissenberg* number and *Reynolds* number.

The shear thinning viscosity curves of monodisperse polystyrene and DNA dilute solutions of different solvent quality and concentration under simple shear flow also show universality.^[12] The power law index is less than 2/3. The critical shear rate, at which the viscosity begins to decrease, increases with the increase of polymer molecular weight. Compared with dilute polymer solutions, semi-dilute unentangled polymer solutions exhibit much larger concentration fluctuation and stronger hydrodynamic interactions between chain segments. After proper normalization, the viscosity curves of semi-dilute unentangled polymer solutions with different concentrations, solvents, and molecular weights under the strong shear flows can still be superimposed into a single power-law exponent master curve, demonstrating universality far away from equilibrium conditions. Moreover, the shear banding could be observed in case of the entangled polymer solution under strong shear flow.^[13,14]

Over the last decades, a great progress has been made on the better understanding of concentration scaling on rheometric properties of monodisperse flexible polymer solutions, noticeably utilising DNA as a highly monodisperse model polymer and molecular conformational probe.^[9,10] However, the effects of polydisperse polymer solutions on such a concentration scaling remain elusive. In this work, industrially relevant polydisperse high molecular weight polyacrylamide aqueous solutions (as a super-good solvent) will be studied under rheometric flow. The concentration dependence of their rheometric properties under both shear and extensional (CaBER) flows will be evaluated. The time-concentration superposition (TCS) principle will be examined for semi-dilute entangled polydisperse high molecular weight polymer solutions and validated in comparison of nearly monodisperse synthetic polymer solutions^[8] and highly monodisperse DNA

solutions.^[9] In Section 2, the experimental methods will be presented. The results and discussion are reported in Section 3 and Section 4, respectively. The conclusions are drawn in Section 5.

EXPERIMENTAL

Polymer Solution

A sample of commercially available polyacrylamide (PAAm) with a nominal weight average molecular weight (M_w) of 18×10^6 g/mol was purchased from Polysciences, Inc. (Catalogue No.: 18522-100) and used as received (here after called as 18M PAAm). Its aqueous solution was prepared by the procedure below. 18M PAAm powder was dissolved in deionised water obtained from the Direct-Q UV-R pure water system after three stages of treatment under room temperature, and in very gentle, continuous stirring for 72 h. It was then put into a 4 °C refrigerator for further homogenization and storage. The average radius of gyration can be estimated by the nominal molecular weight (M) as $R_g = 0.0749M^{0.64 \pm 0.01}(\text{\AA})$ and $R_g = 3295 \text{\AA}$,^[15] the overlap concentration was estimated as $c^* = 0.00946$ wt%, using a simple cubic packing assumption, and the solvent quality parameter, which is a measure from θ solvent ($z=0$) to good solvent condition, is estimated as $z=12.06$,^[16]. Due to lack of the standard high molecular weight polymer sample, quantitative characterization of molecular weight and distribution of 18M PAAm sample by gel permeation chromatography is very difficult if not impossible. However, we may reasonably expect that the polydispersity index of 18M PAAm sample would be significantly higher than 5M PAAm sample of $M_w = 5.7 \times 10^6$ g/mol and $M_w/M_n = 34.4$, supplied by the same source and characterized in our previous work.^[17] A series of highly polydisperse 18M PAAm aqueous solutions were prepared and studied in a semi-dilute entangled concentration range from $10c^*$ (0.1 wt%) to $250c^*$ (2.5 wt%) approximately.

Rheometry

The rheological properties of 18M PAAm aqueous solutions were measured at a constant temperature of 25°C using an ARES-G2 shear rheometer (TA Instruments) and a Capillary Breakup Extensional Rheometer (CaBER, ThermoFisher Scientific). A cone-plate fixture (diameter=50 mm, angle=0.04 rad) was used during the shear measurements. The plate was coupled with an Advanced Peltier System (APS) connected to a ThermoCube Model 10-300 (115/230 V, 50/60 Hz) water bath system with temperature control accuracy of ± 0.2 °C. As for CaBER measurements, plate-plate fixtures were used with a diameter of either 4mm or 6 mm. A circulator package SC 100-A10(0-100) 115V/60Hz was used to set the temperature to 25.0 ± 0.2 °C.

RESULTS

Linear Viscoelasticity

The rheometric properties of 18M PAAm aqueous solutions are measured under 1 Hz oscillatory shear flow by scanning a range of strain amplitude. The results are shown in Figs. 1(a) and 1(b). The plateau values of the storage modulus (G') and of the loss modulus (G'') appear in the low strain amplitude region, corresponding to a linear viscoelasticity zone. As the strain amplitude increases to a certain level, the nonlinear effects

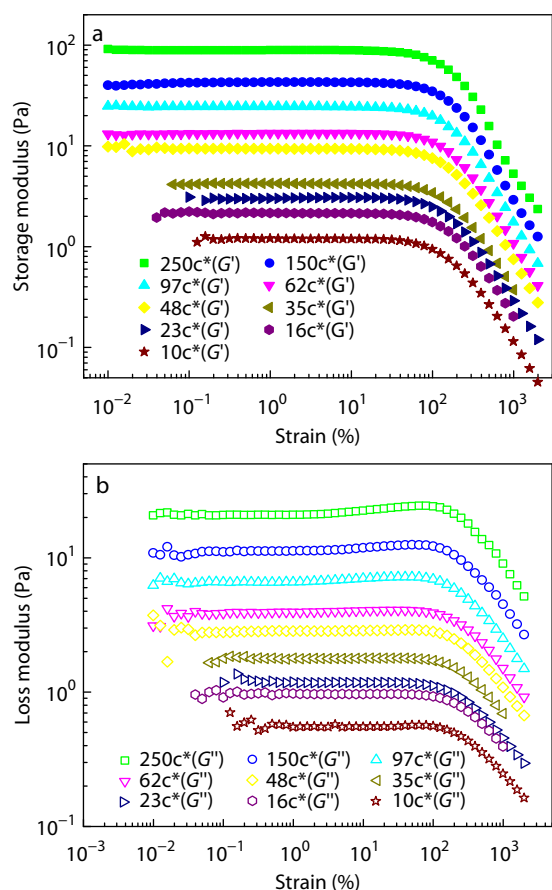


Fig. 1 (a) The storage modulus G' of the 18M PAAm aqueous solutions at various concentration as a function of strain amplitude. (b) The loss modulus G'' of the same solutions as a function of strain amplitude.

occur, G' and G'' decrease. The critical strain amplitude for the occurrence of nonlinear viscoelasticity is almost unchanged. This is due to that the equilibrium or quasi-equilibrium entanglement formed by a portion of very long chains in polydisperse 18M PAAm aqueous solution is established in the relatively low concentration of 10c* and above. The reciprocal of its terminal relaxation time is much lower than the applied frequency. Under such an experimental condition, increasing polymer concentration does not significantly change the critical strain amplitude required to deform entanglement topology and hence to show the nonlinear viscoelasticity. There is a weak overshoot in G'' at high concentrations ($\geq 48c^*$), in which the entanglements with very long relaxation time and hydrogen-bonding complex might behavior like temporary crosslinks, resembling the rheometric feature frequently observed in associated or weakly crosslinked complex fluids.

Within its linear viscoelastic region (small strain amplitude $\gamma < 10\%$), 18M PAAm aqueous solutions with various concentrations were then characterised under the small-amplitude oscillatory shear flow in a range of frequencies under a constant 2% strain amplitude. The results are shown in Fig. 2. As an example, the relaxation spectrum of the 150c* sample was obtained by fitting its data shown in Fig. 2 with an 8-mode generalized Maxwell model, $G'(\omega) = \sum_{i=1}^n \frac{G_i \lambda_i^2 \omega^2}{1 + \lambda_i^2 \omega^2}$;

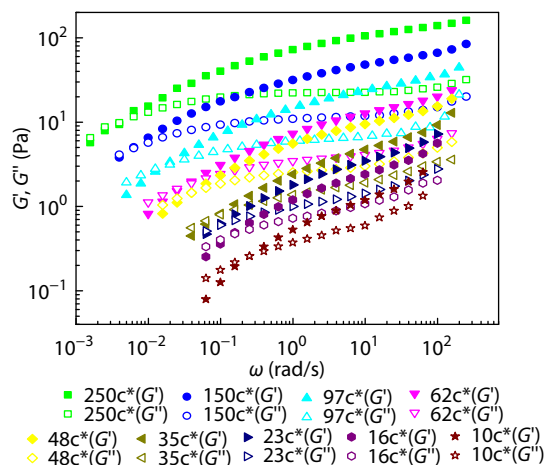


Fig. 2 The storage modulus G' and the loss modulus G'' of the 18M PAAm aqueous solution as a function of angular frequency ω .

$$G''(\omega) = \sum_{i=1}^n \frac{G_i \lambda_i \omega}{1 + \lambda_i^2 \omega^2}, \text{ where } n \text{ is a number of modes, using}$$

IRIS Rheo-hub software. [18] The typical results are shown in Table 1. An excellent fit could be found. The zero-shear viscosity η_0 of higher concentration 18M PAAm aqueous solution (97c*, 150c* and 250c*) was estimated by $\eta_0 = \sum_{i=1}^n G_i \lambda_i + \eta_s$ as shown in Table 2.

Filament Thinning Rheometry

A CaBER rheometer was used for characterisation of the relaxation time of 18M PAAm aqueous solution. The measurements were performed using the 6 mm diameter plates. The initial gap h_0 between the two plates was set to 3 mm, the final gap h_f was 10 mm, giving the Hencky strain of 1.20. The “fast stretch mode” was selected for the tests. The normalized filament diameter D/D_0 versus time of six 18 PAAm aqueous solutions are shown in Fig. 3. The relaxation time, λ_{CaBER} can be estimated by fitting the well-defined exponential decay part of the curves indicated by the straight lines with the expression of $D(t)/D_0 \sim e^{-\frac{t}{\lambda}}$. [19] Higher the concentration, slower the decay of the mid-filament diameter, longer the extensional relaxation time is. The results are shown in Table 2. A comparison is also made with the longest Zimm relaxation time estimated as $\lambda_z = 7.88$ ms according to the well-known Zimm

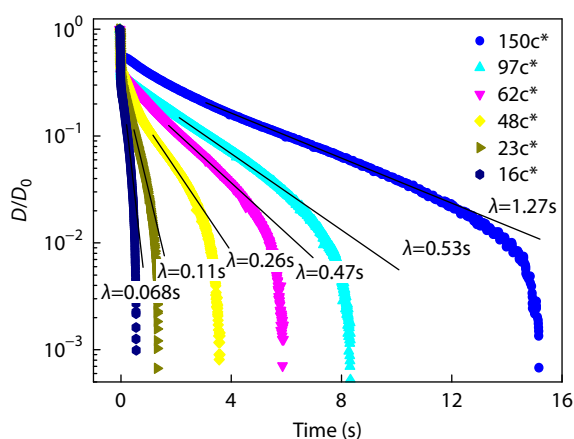
Table 1 The typical relaxation spectrum of 18M PAAm aqueous solution obtained by using IRIS Rheo-hub software. [18]

Modl	150c*			The master curve with $c_{\text{ref}}=48c^*$		
	G_i (Pa)	λ_i (s)	$\eta_i = G_i \lambda_i$ (Pa·s)	G_i (Pa)	λ_i (s)	$\eta_i = G_i \lambda_i$ (Pa·s)
1	36.20	0.003	0.12	9.68	0.0004	0.004
2	13.78	0.03	0.43	5.66	0.005	0.03
3	11.47	0.17	1.99	4.51	0.03	0.13
4	10.59	0.80	8.45	3.65	0.16	0.58
5	10.00	3.57	35.67	2.58	0.80	2.07
6	8.47	16.43	139.10	2.14	3.50	7.49
7	6.23	71.93	448.27	1.46	15.55	22.75
8	4.26	458.4	1951.41	0.91	85.92	77.86
Solvent	—	—	0.001	—	—	0.001
η_0	2585.43			110.92		

Table 2 The relaxation time and the zero-shear viscosity of the 18M PAAm aqueous solutions with a range of concentrations. ^{a–d}

c/c^*	η_0^a (Pa·s)	λ_{CaBER}^b (s)	$\lambda_{\text{CaBER}}/\lambda_z^b$	λ_l^c (s)	λ_c^d (s)
250	9849.9	2.67	338.83	750.43	227.27
150	2585.43	1.27	161.17	625.21	174.79
97	671.56	0.53	67.26	460.67	63.44
62	179.28	0.47	59.64	–	30.68
48	94.18	0.26	32.99	163.86	25.56
35	43.68	0.16	20.30	–	11.21
23	28.26	0.11	13.96	68.65	11.71
16	12.03	0.07	8.88	23.12	7.24
10	4.10	0.04	5.08	–	3.98

^a The zero-shear viscosity η_0 of 150c* and 250c* 18M PAAm aqueous solution was obtained by fitting the data presented in Fig. 2 with the Generalized Maxwell Model and the results of the other concentrations were estimated by the data of steady shear experiments presented in Fig. 6; ^b The relaxation times measured by CaBER rheometer are also shown in comparison of the longest Zimm relaxation time calculated according to the Zimm model for dilute polymer solution; ^c The longest relaxation time λ_l was measured by the shear stress relaxation experiment; ^d The crossover time λ_c was calculated from the crossover frequency at which $G' = G''$ as shown in Fig. 2.

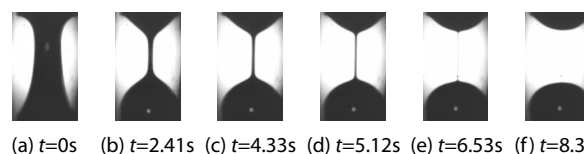
**Fig. 3** The filament diameter decay as a function of time for six 18M PAAm solutions.

model^[20] $\lambda_z \cong \frac{1}{\zeta(3\nu)} \frac{[\eta]M_w\eta_s}{N_A k_B T}$ for dilute polymer solution in a

good solvent, where the intrinsic viscosity $[\eta] = 9.3 \times 10^{-3} M_w^{0.75}$, $\zeta(3\nu) = \sum_i 1/i^\nu$ and $\nu = 0.64$, N_A is the Avogadro's number, k_B is the Boltzmann constant, and T is the absolute temperature. The images of thinning filaments of the 97c* PAAm aqueous solution during stretching were captured by a high-speed camera. Fig. 4(a) shows the filament image of the sample after the completion of pre-stretching. Figs. 4(b)–4(e) show the snapshots of the thinning filament at the specified instants. Fig. 4(f) shows the filament at the break up stage. The higher the concentration, the longer the time taken for the filament breakage.

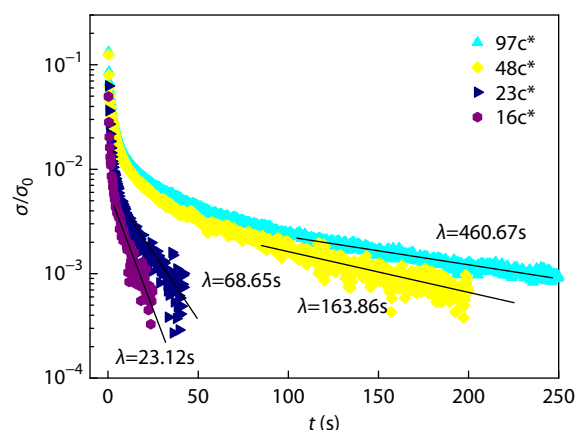
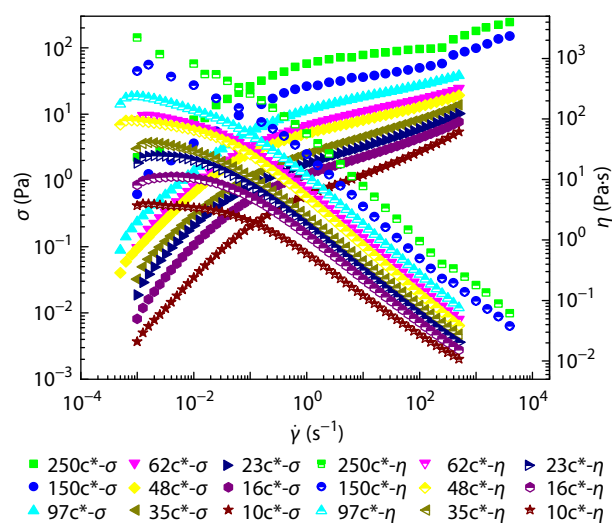
Non-linear Shear Rheology

The longest relaxation time of polymer solutions can be quantified by the stress relaxation experiment. In order to deform the entangled 18M PAAm aqueous solutions completely out of equilibrium structure, a sufficiently high shear rate was imposed to the testing samples till the steady state was reached. The shear flow was then stopped and the shear stress

**Fig. 4** The snapshots of the filament thinning of the 97c* 18M PAAm solution at the specified instants.

relaxation was measured. The longest relaxation time was estimated by fitting the stress relaxation data in a form of exponential decay as indicated by the straight lines in Fig. 5, with the expression of $\sigma(t) \sim \exp(-t/\lambda_l)$. The results have been verified to ensure that the estimated relaxation time of the sample is independent of the imposed shear rate. Fig. 5 shows the results of 97c*, 48c*, 23c* and 16c* PAAm aqueous solutions after 600 second pre-shear at a shear rate of 100 s^{-1} . Clearly, the rate of stress relaxation is reduced as PAAm concentration is increased. The estimated relaxation times (λ_l) of these PAAm aqueous solutions are listed in Table 2 and show the concentration dependence.

All the samples are also characterized by the steady shear

**Fig. 5** The normalized stress σ/σ_0 as a function of time for the 18M PAAm aqueous solutions of $c/c^* = 97, 48, 23, 16$, respectively.**Fig. 6** Steady shear stress σ and viscosity η as a function of the shear rate for semi-dilute 18M PAAm aqueous solutions.

experiment. In Fig. 6, the measured steady shear stresses are plotted as a function of shear rates for a series of 18M PAAm aqueous solutions from $10c^*$ to $250c^*$, respectively. As the concentration is increased, the slope of the steady shear stress curves in the shear rate region between 0.5 and 100 s^{-1} is decreased. The shear thinning exponent of steady viscosity show some concentration dependence.

DISCUSSION

Under the isobaric condition, two thermodynamic state variables, namely polymer concentration and solvent quality, are sufficient to define the equilibrium or quasi-equilibrium properties of monodisperse flexible neutral chain polymer solutions.^[21,22] Water is considered as a “super-good solvent” for PAAm due to its high value of the solvent quality ($z=12.06$). The power law scaling exponent of the radius of gyration of PAAm chain in water with respect to its molecular weight in a finite range of molecular weight is 0.64 , which is significantly higher than the asymptotic value of 0.588 for sufficiently high molecular weight polymer in good solvent. The present work systematically evaluates the concentration dependence of the linear and nonlinear rheological properties of highly polydisperse 18M PAAm aqueous solutions under the fixed super-good solvent condition. The concentration dependence of their characteristic relaxation time is analyzed on the basis of (i) the crossover time λ_c calculated from the crossover frequency at which $G'=G''$ as shown in Fig. 2; (ii) the longest relaxation time λ_l from the shear stress relaxation experiment and (iii) the elongational relaxation time measured from CaBER experiments λ_{CaBER} . As presented in Fig. 7, there is a power law concentration scaling in a form of $\lambda_c \sim (c/c^*)^{1.21 \pm 0.09}$, $\lambda_l \sim (c/c^*)^{1.14 \pm 0.10}$, $\lambda_{\text{CaBER}} \sim (c/c^*)^{1.31 \pm 0.03}$, respectively. Over the semi-dilute entangled region from $10c^*$ to $250c^*$, the scaling exponents of 18M PAAm aqueous solutions are significantly smaller than what predicted by the dynamic scaling theory^[5] and observed in the semi-dilute entangled polymer and DNA solutions, which are scaled as $\lambda_c \sim (c/c^*)^{3.5 \pm 0.5}$, $\lambda_l \sim (c/c^*)^{2.15 \pm 0.05}$ for good solvent and $\lambda_l \sim (c/c^*)^{3.1 \pm 0.2}$ for θ solvent, respectively.^[7,9] The difference attributes to the super-good solvent condition and very high polydispersity of 18M PAAm aqueous solutions.

As shown in Fig. 8, the plateau modulus estimated by the Wu method^[23] for 18M PAAm solution (assumed $M_w/M_n=50$) is scaled with the concentration as $G_N^0 \sim (c/c^*)^{1.11 \pm 0.04}$. The results are insensitive to the polydispersity index for $M_w/M_n > 34$. Constraint-release becomes much more pronounced for highly polydisperse polymer solutions, within which the relaxation of a long chain is accelerated by release of the entanglements it has with the shorter, faster relaxing chains around it. Hence, the scaling exponent is significantly smaller than the exponents predicted by the dynamic scaling theory^[5] for semi-dilute entangled monodisperse polymer solutions, which are scaled as $G_N^0 \sim (c/c^*)^{2.3}$ for good solvent and $G_N^0 \sim (c/c^*)^{7/3}$ for θ solvent, respectively. The concentration scaling of the zero-shear viscosity η_0 is also shown in Fig. 8 and is expressed in a form of $(\eta_0 - \eta_s) \sim (c/c^*)^{2.4 \pm 0.1}$ over the concentration region studied. Such a scaling could also be estimated approximately by the concentration scaling of G_N^0 and λ_c characterised experimentally shown in Figs. 7 and 8 as

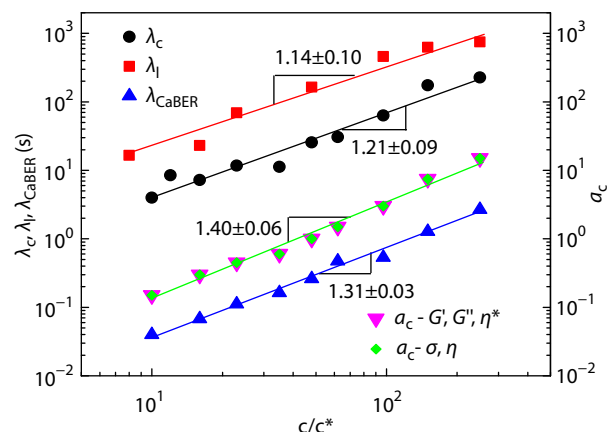


Fig. 7 The concentration scaling of the relaxation times λ_c , λ_l , λ_{CaBER} and the shifting factor a_c ($c_{\text{ref}}=48c^*$) to obtain the master curves of G' , G'' and η^* in Fig. 10, and the master curve of steady shear viscosity η and shear stress σ in Fig. 12 for semi-dilute 18M PAAm aqueous solutions.

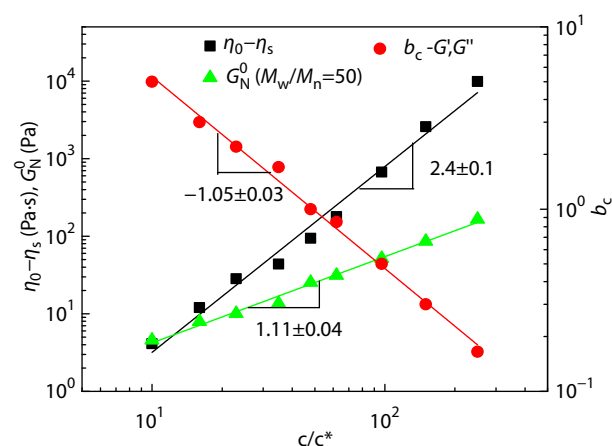


Fig. 8 The concentration scaling of the zero-shear viscosity η_0 , the plateau modulus G_N^0 and the shifting factor b_c ($c_{\text{ref}}=48c^*$) to obtain the master curves of G' , G'' and η^* in Fig. 10 for the semi-dilute entangled 18M PAAm aqueous solutions.

$\eta_0 - \eta_s \approx G_N^0 \lambda_c \sim (c/c^*)^{2.32 \pm 0.09}$. The concentration scaling exponents of the zero-shear viscosity obtained from the different methods are approximately agreed each other and significantly higher than that of unentangled neutral polymers in good solvent, but lower than that of entangled neutral polymers and DNA in good solvent.^[8,9] Since only a portion of PAAm chains exceeded the entanglement molecular weight could play an active role in the entanglement dynamics and the entanglement molecular weight is decreased as the concentration is increased, the smaller scaling exponent is likely caused by broader molecular weight distribution of 18M PAAm solution. The overall effect would be a weaker concentration scaling in comparison to monodisperse polymer solutions.

In order to examine the applicability of the classical Cox-Merz rule, the plots of the complex viscosity curve $\eta^*(\omega)$ obtained from the data of Fig. 2 under small angle oscillatory shear experiment and the steady shear viscosity curve $\eta(\dot{\gamma})$ obtained from the data of Fig. 6 under steady shear experi-

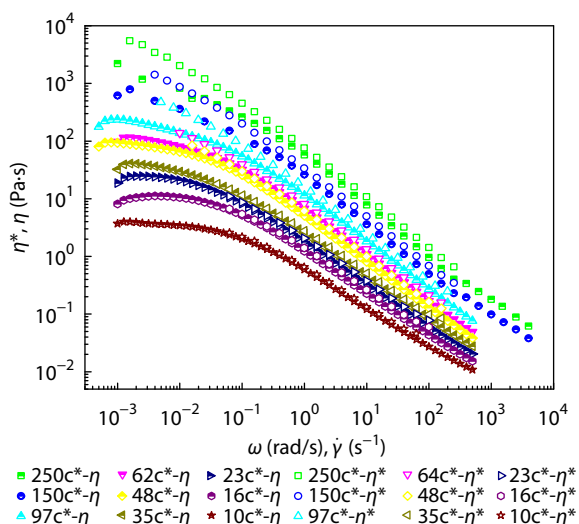


Fig. 9 The overlay plots of the complex viscosity curve $\eta^*(\omega)$ (the open triangles) and the steady shear viscosity curve $\eta(\dot{\gamma})$ (the filled triangles).

ment are overlaid as shown in Fig. 9. The Cox-Merz rule is approximately held in the concentration range from $10c^*$ to $35c^*$. For the concentration higher than $35c^*$, the steady shear viscosity over a range of shear rate is significantly deviated from the complex viscosity over the equivalent range of the scanned frequency. Therefore, the steady shear rheometric properties cannot be reliably predicted by their linear viscoelastic properties.

In analogy to the time-temperature superposition (TTS) principle, the concentration dependence of the rheometric properties of polymer solutions can be analyzed by applying the TCS procedure to the data presented in Fig. 2. With respect to an arbitrary reference concentration (set as $48c^*$ here), a master curve of storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) could be obtained by shifting their linear viscoelastic data horizontally by a factor a_c and vertically by a factor b_c , respectively. The results are shown in Fig. 10. The same shift factor a_c and b_c were applied to obtain the master curves of G' , G'' in Fig. 10(a) and η^* in Fig. 10(b). They exhibit a power law concentration scaling as $a_c \sim (c/c^*)^{1.40 \pm 0.06}$ and $b_c \sim (c/c^*)^{-1.05 \pm 0.03}$ as shown in Fig. 7 and Fig. 8, respectively. The concentration scaling exponent of the shifting factor a_c is slightly higher than the scaling exponent of λ_c . The difference is probably caused by the relatively low ratio of signal and noise in the pointwise measurements of λ_c in the low frequency range as shown in Figs. 2 and 7, from which would produce a systematic error in comparison of the results of a_c based on the superposition of the entire spectrum curves.

The shear-thinning exponent of complex viscosity in its master curve is -0.73 ± 0.04 in the intermediate frequency region and -0.84 ± 0.05 in high frequency region, respectively. The exponent in high frequency is close to the universal exponent of 0.85 for concentrated monodisperse polymer solutions and melts.^[24] The master curve in the high frequency region is mainly composed of the shifted data of higher concentration. The master curves could be well-fitted by the 8-mode generalized Maxwell model using IRIS Rheo-hub soft-

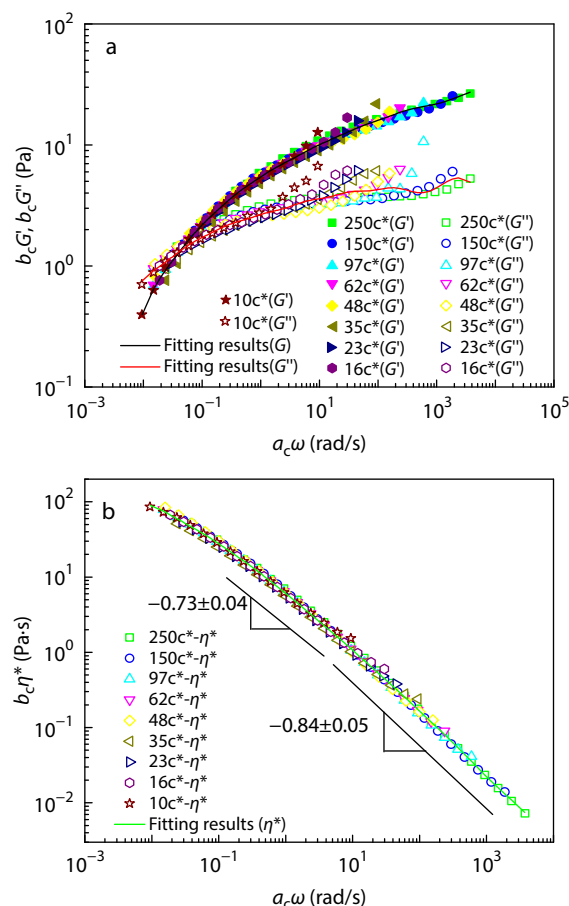


Fig. 10 (a) A master curve of storage modulus (G') and loss modulus (G''); (b) A master curve of complex viscosity (η^*) after shifting the linear viscoelastic data of the semi-dilute 18M PAAm solutions horizontally by a factor a_c and vertically by a factor b_c , with respect to $c_{ref}=48c^*$. The lines are fitted by the 8-mode generalized Maxwell model using IRIS Rheo-hub software^[18] and the relaxation spectrum is listed in Table 1.

ware^[18] as shown in Fig. 10, within which the relaxation spectrum is listed in Table 1.

By closely examining in Fig. 10(a), the shifted storage and loss moduli of various concentrations are not so well superimposed in the high frequency region. It reflects the fact that in semi-dilute entangled polymer solutions, the concentration scaling of Rouse dynamics is different from the terminal flow dynamics dominated by the entanglement dynamics. The TCS could only be realized either in the terminal dynamic regime or in the Rouse regime. In the present work, the choice of the superposition over the terminal region would result in less well superimposed high frequency data as also observed in the monodisperse DNA and other polymer solutions.^[9,25]

If considering the shifting factors a_c and b_c as a reduced frequency (or equivalently an inverse of a characteristic time) $a_c \sim 1/\omega_c \approx \lambda_c$ and a reduced modulus $b_c \sim 1/G_N^0$, respectively, the ratio of the shifting factors could be related to the zero-shear viscosity and scaled with polymer concentration as $(a_c/b_c) \sim \lambda_c G_N^0 \approx (\eta_0 - \eta_s) \sim (c/c^*)^{2.45 \pm 0.06}$. Fig. 11 plots (a_c/b_c) as a function of (c_{ref}/c) in the logarithmic scales. The plot exhibits a well-defined power law scaling with the exponent of

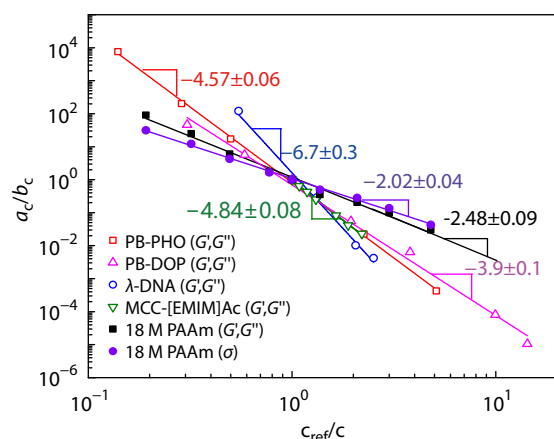


Fig. 11 A plot of (a_c/b_c) as a function of (c_{ref}/c) in the logarithmic scales for highly polydisperse 18M PAAm in water (super-good solvent) with $c_{ref}=48c^*$, nearly monodisperse polybutadiene (PB) in phenyloctane (PHO, good solvent) with $c_{ref}=56c^*$ and in dioctyl phthalate (DOP, θ solvent) with $c_{ref}=44.3c^*$,^[8] highly monodisperse 31.5M DNA in Tris-EDTA buffer solution (good solvent) with $c_{ref}=49.1c^*$,^[9] and the microcrystalline cellulose (MCC) in [EMIM]Ac (ionic liquid under θ condition at 25 °C) with $c_{ref}=19.5c^*$,^[26] respectively.

-2.48 ± 0.09 , which actually resembles the concentration scaling exponent of the zero-shear viscosity. Moreover as shown in Fig. 11, it has been validated that the linear viscoelasticity data $G'(\omega)$ and $G''(\omega)$ reported in the literature for other monodisperse and polydisperse polymer solutions over a range of concentrations and in different solvent quality under a fixed temperature could be superimposed into a master curve respectively, including nearly monodisperse polybutadiene (PB) in phenyloctane (good solvent) and in dioctyl phthalate (θ solvent),^[8] and highly monodisperse DNA in Tris-EDTA buffer solution as a super entangled model polymer in good solvent,^[9] and polydisperse microcrystalline cellulose (MCC) with a polydispersity index of 12 in 1-ethyl-3-methylimidazolium acetate ([EMIM]Ac) (ionic liquid).^[26] The results show that the TCS principle is applicable to a wide range of polymer solutions as long as an adequate power law concentration scaling of the shifting factors could be identified. The concentration change of entangled polymer solution could be considered as to effectively shift its average characteristic time. The rheometric properties of polymer solutions with higher concentration are equivalent to the higher frequency properties of less concentrated polymer solutions. The concentration scaling of the shifting factors (a_c/b_c) is dependent on polymer polydispersity as well as solvent quality (ionic strength), dynamic regime and possibly molecular weight. In comparison with the monodisperse polymer solution in good solvent, the polydispersity and super-good solvent condition of 18M PAAm aqueous solutions significantly reduce the concentration scaling exponent of the shifting factors (a_c/b_c) .

The TCS principle is also extended in the analysis of concentration dependence of the steady shear viscosity and steady stress of semi-dilute entangled polydisperse 18M PAAm aqueous solutions. By choosing $c_{ref}=48c^*$ and using appropriate shift factors a_c and b_c , the steady shear viscosity curves could be superimposed as shown in Fig. 12(a). The

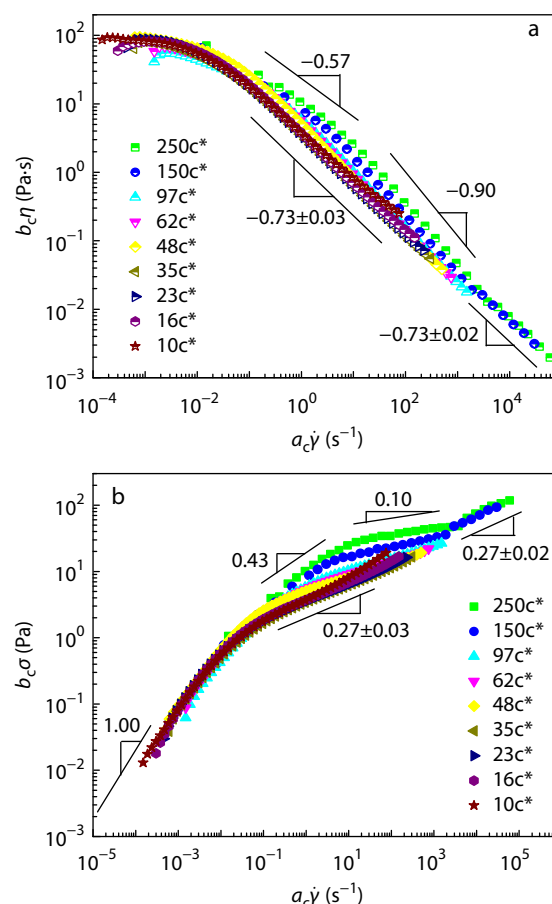


Fig. 12 (a) A master curve of steady shear viscosity; (b) A master curve of steady shear stress after shifting the steady shear rheometric data of the semi-dilute 18M PAAm solutions horizontally by a factor a_c and vertically by a factor b_c , with respect to $c_{ref}=48c^*$.

suitable horizontal shifting factors a_c for the superposition of the steady rheometric properties have little difference from those used for the construction of the master curves in Fig. 10. However, the different vertical shift factors b_c are required due to the difference of the linear and nonlinear viscoelastic response to shear flow, especially for 18M PAAm solution in higher concentrations, where the Cox-Merz rule is invalid. As a consequence of the above shifting procedure for steady shear viscosity, the steady shear stress curves are superimposed as shown in Fig. 12(b). Fig. 11 shows a power law concentration scaling of the shifting factors (a_c/b_c) for the superposition of steady shear viscosity and shear stress with a significantly decreased exponent of 2.02 ± 0.04 , in comparison of the scaling exponent of the linear rheometric properties of the same solutions and other monodisperse semi-dilute entangled polymer solutions in good solvents. The results provide some useful physical insight into the concentration dependence of steady shear viscosity and shear stress in the nonlinear flow regime as discussed below.

In the linear shear flow region ($\dot{\gamma}a_c < 2.0 \times 10^{-3} \text{ s}^{-1}$), there is a well-defined zero-shear viscosity. The shear stress increases linearly with shear rate. The rheometric properties of highly polydisperse polymer solutions can be superimposed into a master curve. Their concentration dependence is consistent

with the concentration scaling of the relaxation times and the zero-shear viscosity over the semi-dilute entangled concentration region of 18M PAAm aqueous solutions.

In the nonlinear shear thinning flow region, there is still no clear consensus in the literature on the shear-thinning exponent of the steady shear viscosity with shear rate for monodisperse polymer solutions. The experimental results show that it varies from a low value of about 0.1 for very dilute solutions up to about 0.85 for concentrated entangled polymer solutions and melts.^[12,24] The comprehensive rheometric characterizations of semi-dilute entangled polydisperse high molecular weight polymer solutions in good solvent over a wide range of concentrations are still scarce. As shown in Fig. 12, the steady shear viscosity and shear stress of 18M PAAm aqueous solutions with relatively lower concentration ($\leq 35c^*$) could be superimposed into a master curve with the shear-thinning exponents of 0.73 ± 0.03 and 0.27 ± 0.03 , respectively, over a wide range of shear rates in about six decades. It is in good agreement with the master curve of complex viscosity over the intermediate frequency range shown in Fig. 10(b).

For higher concentration 18M PAAm solutions ($\geq 48c^*$), the effects of concentration are much more pronounced. Both the steady shear viscosity and shear stress of these higher concentration solutions cannot be superimposed into a master curve. In such a relatively high concentration range, the coupling and competition between the various mechanisms of entanglement dynamics including reptation, contour length fluctuation, tube dilation, convective constraint release, conformational stretch, etc., would become more complex. The mixing rule of polydisperse polymer solutions under flow condition is still an unsolved issue in understanding of entanglement dynamics. Some loosely formed entanglements can be easily disentangled by shear flow. The overall entanglement network could be weakened further as shear rate is increased. Hence their rheometric properties under flow condition depend on the survivability of the entanglements formed by chain molecules with different lengths, in turn affected significantly by polymer concentration, which results in the failure of the superposition at higher concentrations ($\geq 48c^*$). However, it is worthwhile under the TCS framework to analyze a general trend of the concentration scaling of the nonlinear rheometric properties and the dependence of the shear-thinning exponent on concentration and the scaled shear rate in three flow regions.

In the transition region from the linear shear flow to the shear thinning flow ($2.0 \times 10^{-3} \text{ s}^{-1} < \dot{\gamma} a_c < 30 \text{ s}^{-1}$), the shear thinning exponent gradually reduces as shear rate increases. The level of the reduction depends on polymer concentration. The asymptotic shear thinning exponents are varied between 0.73 and 0.57 for lower ($\leq 35c^*$) and higher concentration ($\geq 48c^*$) solutions, respectively. The scaling exponents for shear stress are also enveloped between 0.27 and 0.43.

In the relatively higher shear rate region ($30 \text{ s}^{-1} < \dot{\gamma} a_c < 3000 \text{ s}^{-1}$), the upper bounded shear thinning exponents of the superimposed shear viscosity and shear stress of 18M PAAm solutions with higher concentration are increased to 0.90 and decreased to 0.10, respectively. It is also consistent with the shear-thinning exponent of complex viscosity in high frequency shown in Fig. 10(b), in which the data points are mainly composited of the complex viscosity of the solutions

with higher concentrations. Further increasing polymer concentration, the shear-thinning exponents of shear viscosity and shear stress would ultimately approach to the upper bounded scaling exponents of 1.0 and 0.0, respectively, as shown by computer simulation for polymeric melts.^[27]

In the much higher shear rate region ($\dot{\gamma} a_c > 3000 \text{ s}^{-1}$), the lower bounded value of the shear thinning exponents observed in the relatively less concentrated ($\leq 35c^*$) 18M PAAm solutions is recovered, i.e., 0.73 ± 0.02 for shear viscosity and 0.27 ± 0.02 for steady shear stress, respectively. The chain molecules in a relatively high concentration semi-dilute solution would experience a flow environment like in a less concentrated polymer solution. As the entanglement density is reduced, the effects of polymer concentration tend to be small in strong shear flow regime. Such a universal scaling behaviour is consistent with the experimental observation by molecular fluorescence microscopy techniques.^[10,11] Therefore the concentration effects of polydisperse polymer solutions could be greatly reduced by the dynamic "molecular individualism" in strong flow.^[11]

CONCLUSIONS

The concentration scaling on linear and nonlinear rheological properties of highly polydisperse polymer solutions has been studied systematically by rheometric characterisation of semi-dilute 18M PAAm aqueous solutions with concentration varying from $10c^*$ to $250c^*$. The results show a well-defined concentration scaling of the characteristic relaxation time, the plateau modulus and the zero-shear viscosity across the semi-dilute entangled concentrations. The scaling exponent of highly polydisperse entangled polymer solutions is significantly smaller than the exponent of the monodisperse entangled polymer solutions in good solvents.

The TCS principle has been verified in analysis of the linear and nonlinear rheometric properties of semi-dilute entangled 18M PAAm aqueous solutions. The linear viscoelastic properties such as storage modulus, loss modulus and complex viscosity could be superimposed into a master curve in the terminal dynamic regime for a wide range of polymer solutions as long as an adequate power law concentration scaling of the shifting factors could be identified. The concentration scaling exponent of the shifting factors for highly polydisperse polymer solutions significantly reduces in comparison with the scaling exponent of monodisperse polymer solutions. It is also dependent on solvent quality (ionic strength), dynamic regime and possibly molecular weight. The steady viscosity and shear stress of relatively low concentration ($\leq 35c^*$) 18M PAAm solutions could be superimposed into a master curve with the shear-thinning exponent of 0.73 and 0.27, respectively, over a shear rate range about six orders of magnitudes.

In the intermediate nonlinear flow regime, the rheometric properties of polydisperse polymer solutions with higher concentration ($\geq 48c^*$) cannot be superimposed into a master curve and show a pronounced concentration dependence. The shear thinning exponent of steady shear viscosity firstly changes from 0.73 to 0.57 as concentration increases, and then increases from 0.57 to 0.90 under sufficiently high shear rate.

Under even stronger shear flow, the shear thinning exponents of all the solutions with different concentrations are converged to the lower bounded value, which is a universal feature of relatively low concentration 18M PAAm solutions, i.e., 0.73 ± 0.02 for shear viscosity and 0.27 ± 0.02 for steady shear stress, respectively. The effects of concentration on the scaling exponent tend to be small. The hydrodynamic interaction is the key factor that governs the dynamic evolution of polymer conformation in terms of the "molecular individualism" and concentration dependence of the rheometric properties of semi-dilute polymer solutions. As long as a well-defined concentration scaling of the shifting factors could be identified, the TCS principle is applicable in analysis of the linear and nonlinear rheometric properties of semi-dilute entangled highly polydisperse polymer solutions. It would provide a better physical insight in dynamic modelling of semi-dilute entangled polymer solutions in turbulence drag reduction and elastic turbulence.

NOTES

The authors declare no competing financial interest.

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