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Theory of viscoelastic properties of polyelectrolyte solutions

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Abstract

A theory of frequency dependence of shear viscosity η and modulus G of polyelectrolyte solutions is presented as functions of concentrations of the polymer (c) and added salt. In the asymptotic limit of high frequency ω, η is proportional to $c\omega^{-2/3}$ in dilute solutions and to $c^{3/4}\omega^{-1/2}$ in semidilute solutions under salt-free conditions. As in the zero-frequency limit, reduced viscosity η and reduced modulus G are decreasing functions of c in salt-free semidilute solutions at high frequencies: $\eta_r \sim c^{-1/4}\omega^{-1/2}$, $G_r \sim c^{-1/4}\omega^{1/2}$. If the salt concentration is high, $\eta \sim c\omega^{-4/9}$ in dilute solutions and $\eta \sim c^{9/8}\omega^{-1/2}$ in semidilute solutions, as expected for neutral good solutions. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

We extend our earlier theory [1] of dynamics of polyelectrolyte solutions to the frequency ω dependence of shear viscosity $\eta(\omega)$ and shear modulus $G(\omega) = \mathrm{i}\omega\eta(\omega)$. In infinite dilute solutions, the intrinsic viscosity $[\eta]$ is given by [2]

$$[\eta] = \frac{\mathrm{R}T}{M\eta_0}\sum_{j=1}^{N}\frac{\tau_j}{1+\mathrm{i}\omega\tau_j} \tag{1}$$

where R, T, M, η_0, and τ_j are respectively the gas constant, absolute temperature, molecular weight (proportional to the number of Kuhn segments N per chain), shear viscosity of the solvent, and relaxation time of the jth Rouse–Zimm mode. The intrinsic storage $[G']$ and loss $[G'']$ moduli are

$$\begin{aligned}[G'] &= \frac{\mathrm{R}T}{M}\sum_{j=1}^{N}\frac{\omega^2\tau_j^2}{(1+\omega^2\tau_j^2)}\\ [G''] &= \frac{\mathrm{R}T}{M}\sum_{j=1}^{N}\frac{\omega\tau_j}{(1+\omega^2\tau_j^2)}\end{aligned} \tag{2}$$

The asymptotic laws of frequency dependencies of η and G for different polyelectrolyte concentrations and salt concentrations are readily obtained and are presented in Table 1. Since the basic theory of polyelectrolyte dynamics is already outlined, only the most important steps necessary to perform the extension in the current study will be mentioned below and the details of the calculation may be found in Ref. [1].

2. Theory

We consider a solution containing monodisperse uniformly charged polyelectrolyte chains each of N Kuhn segments in a medium with neutralizing counterions and known amount of added salt. In our theory, the counterions and dissociated salt ions appear as the Debye length. By accounting for chain connectivity, the coupled screenings of excluded volume, electrostatic interaction, and the electrostatic coupling between polyelectrolytes and counterions, the viscosity $\eta(\omega)$ of the solution is given in Refs. [1,3]

$$\eta(\omega) - \eta_0 = \lim_{k\to 0}\frac{1}{k^2}(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}})\cdot\Sigma(\mathbf{k},\omega) \tag{3}$$

where

$$\Sigma(\mathbf{k},\omega) = \mathbf{1}\frac{cl}{\pi}\int_{2\pi/Nl}^{\infty}\mathrm{d}qS(\mathbf{k},q,\omega)J^{-1}(q,\omega) \tag{4}$$

$$J(q,\omega) = \int\frac{\mathrm{d}\mathbf{j}}{(2\pi)^3}\frac{\mathbf{1}-\hat{\mathbf{j}}\hat{\mathbf{j}}}{[\mathbf{1}(\eta_0 j^2 + \mathrm{i}\omega) + \Sigma(\mathbf{j},\omega)]}S(\mathbf{j},q,\omega) \tag{5}$$

$$S(\mathbf{k},q,\omega) = \int_{-\infty}^{\infty}\mathrm{d}t\int_{-\infty}^{\infty}\mathrm{d}(s-s')^{\mathrm{i}\omega t+\mathrm{i}q(s-s')} \times\langle\exp(\mathrm{i}\mathbf{k}\cdot[\mathbf{R}(s,t)-\mathbf{R}(s',0)])\rangle \tag{6}$$

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Table 1
Dependencies of viscosity and modulus in unentangled dilute and semidilute solutions on c, N, and ω for low and high salt conditions. ν is the radius of gyration exponent in infinitely dilute solutions

		Dilute		Semidilute	
	Salt level	$\omega \to 0$	$\omega \to \infty$	$\omega \to 0$	$\omega \to \infty$
$\frac{\eta - \eta_o}{\eta_o}$		$\mathrm{c}\mathrm{N}^{3\nu-1}$	$c\omega^{-\frac{(3\nu-1)}{3\nu}}$	$c^{\frac{1}{(3\nu-1)}}N$	$\omega^{-\frac{1}{2}}c^{\frac{3\nu}{2(3\nu-1)}}$
	Low salt	$\mathrm{c}\mathrm{N}^2$	$c\omega^{-\frac{2}{3}}$	$c^{\frac{1}{2}}N$	$\omega^{-\frac{1}{2}}c^{\frac{3}{4}}$
	High salt	$cN^{\frac{4}{5}}$	$c\omega^{-\frac{4}{9}}$	$c^{\frac{5}{4}}N$	$\omega^{-\frac{1}{2}}c^{\frac{9}{8}}$
$\frac{G - G_o}{G_o}$		$\omega \mathrm{c}\mathrm{N}^{3\nu-1}$	$c\omega^{\frac{1}{3\nu}}$	$\omega c^{\frac{1}{3\nu-1}}N$	$\omega^{\frac{1}{2}}c^{\frac{3\nu}{2(3\nu-1)}}$
	Low salt	$\omega \mathrm{c}\mathrm{N}^2$	$c\omega^{\frac{1}{3}}$	$\omega c^{\frac{1}{2}}N$	$\omega^{\frac{1}{2}}c^{\frac{3}{4}}$
	High salt	$\omega cN^{\frac{4}{5}}$	$c\omega^{\frac{5}{9}}$	$\omega c^{\frac{5}{4}}N$	$\omega^{\frac{1}{2}}c^{\frac{9}{8}}$

where $\mathbf{k}$ is the scattering wave vector, $\hat{\mathbf{k}}$ the unit vector along $\mathbf{k}$, $q = (2\pi p/Nl)$ the Rouse mode (with $p = 0, 1, 2, 3, \ldots$), $\mathbf{R}(s,t)$ is the position vector of sth monomer at time t, l is the Kuhn length, and c is the monomer concentration of the polyeletrolyte. In obtaining the above expression, entanglement effects are ignored and so we consider the crossover from the Zimm regime at infinitely dilute solutions to the Rouse regime in unentangled semidilute solutions. The key results are summarized in Table 1.

3. Results

(i) Dilute: For dilute solutions the leading term of J follows from Eq. (5) as

$$J(q,\omega) = \int \frac{\mathrm{d}\mathbf{j}}{(2\pi)^3}\,\frac{(\mathbf{1} - \hat{\mathbf{j}}\hat{\mathbf{j}})}{[\mathbf{1}(\eta j^2 + \mathrm{i}\omega)]}\,\frac{\left(\frac{j^2 l_1}{3}\right)}{\left[\left(\frac{j^2 l_1}{6}\right)^2 + q^2\right]} \tag{7}$$

where the frequency dependence of the structure factor $S(\mathbf{j},q,\omega)$ is ignored and l_1 is the effective step length (the polyelectrolyte chain being taken as an effective Gaussian chain) given in Ref. [4]

$$l_1 \sim q^{1-2\nu} \sim N^{2\nu-1} \tag{8}$$

with ν being the radius of gyration exponent describing the molecular weight dependence of the radius of gyration R_g,

$$R_g \sim N^{\nu}. \tag{9}$$

ν approaches 3/5 and 1, respectively, for high salt and low salt conditions.

In the low frequency limit, Eqs. (3–8) lead to the familiar Zimm law [1]

$$\frac{\eta - \eta_o}{\eta_o} \sim cN^{3\nu-1} \tag{10}$$

and

$$\tau_q \sim q^{-3\nu}. \tag{11}$$

In the high frequency limit, the intrinsic viscosity follows from Eq. (1) as

$$[\eta] \sim \int \mathrm{d}q \frac{\tau_q}{(1 + \mathrm{i}\omega\tau_q)} \tag{12}$$

so that both the real and imaginary parts are proportional to

$$[\eta] \sim \omega \int \mathrm{d}q \frac{1}{q^{6\nu} + \omega^2} \sim \omega^{-\frac{(3\nu-1)}{3\nu}} \tag{13}$$

Eq. (2) gives the intrinsic modulus as

$$[G] \sim \omega^{\frac{1}{3\nu}}. \tag{14}$$

(ii) Semidilute: A self-consistent evaluation of Σ as discussed in Ref. [1] for high enough concentrations (c greater than the overlap concentration $c^* \sim N^{1-3\nu}$) with full hydrodynamic screening and without entanglement effects yields [1,5]

$$\tau_q \sim c^{\frac{(2-3\nu)}{(3\nu-1)}} q^{-2}. \tag{15}$$

Substitution of this result either in Eq. (1) or Eq. (3) results in the Rouse law at zero frequency,

$$\frac{\eta - \eta_o}{\eta_o} \sim c^{\frac{1}{3\nu-1}} N. \tag{16}$$

At high frequencies,

$$\frac{\eta - \eta_o}{\eta_o c} \sim \omega \int \mathrm{d}q \frac{\tau_q^2}{(1 + \omega^2 \tau_q^2)} \sim \frac{1}{\sqrt{\omega}} c^{\frac{(2-3\nu)}{2(3\nu-1)}} \tag{17}$$

and

$$\frac{G - G_o}{G_o c} \sim \sqrt{\omega} c^{\frac{(2-3\nu)}{2(3\nu-1)}}. \tag{18}$$

Therefore in this Rouse regime of unentangled semidilute solutions where hydrodynamic interaction is screened, both the reduced viscosity and reduced modulus decrease with increase in polymer concentration in salt-free solutions ($\nu \to 1$),

$$\frac{\eta - \eta_o}{\eta_o c} \sim \begin{cases} Nc^{-\frac{1}{2}}, & \omega \to 0 \\ \omega^{-\frac{1}{2}} c^{-\frac{1}{4}}, & \omega \to \infty. \end{cases} \tag{19}$$

and

$$\frac{G - G_o}{G_o c} \sim \begin{cases} \omega N c^{-\frac{1}{2}}, & \omega \to 0 \\ \omega^{\frac{1}{2}} c^{-\frac{1}{4}} & \omega \to \infty. \end{cases} \tag{20}$$

These apparent strange results are to be contrasted with the results at high salt concentrations ($\nu \to 3/5$),

$$\frac{\eta - \eta_o}{\eta_o c} \sim \begin{cases} Nc^{\frac{1}{4}}, & \omega \to 0 \\ \omega^{-\frac{1}{2}} c^{\frac{1}{8}}, & \omega \to \infty. \end{cases} \tag{21}$$

and

$$\frac{G - G_o}{G_o c} \sim \begin{cases} \omega N c^{\frac{1}{4}}, & \omega \rightarrow 0 \\ \omega^{\frac{1}{2}} c^{\frac{1}{8}}, & \omega \rightarrow \infty. \end{cases} \quad (22)$$

The above general results and the asymptotic values for high and low salt concentrations are included in Table 1. The zero-frequency results are already known in the literature [1,5].

4. Conclusions

The frequency dependence of shear viscosity and shear modulus of a polyelectrolyte solution is derived for dilute and semidilute solutions at different concentrations of added salt. Although several experimental studies [6–8] have been reported on η,G, and the compliance of polyelectrolyte solutions, systematic investigations on the frequency dependence is still lacking. We hope calculations presented in this paper will stimulate further experimental efforts in understanding polyelectrolyte dynamics.

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References

[1] Muthukumar M. J Chem Phys 1997;107:2619.
[2] Ferry J. Viscoelastic properties of polymers. New York: Wiley, 1980.
[3] Muthukumar M. J Chem Phys 1985;83:3161.
[4] Muthukumar M. J Chem Phys 1996;105:5183.
[5] Dobrynin AV, Colby RH, Rubinstein M. Macromolecules 1995;28:1859.
[6] Hodgeson DF, Amis EJ. J Chem Phys 1991;94:4581.
[7] Takahashi Y, Hase H, Yamaguchi M, Noda I. J Non-Cryst Solids 1994;172–174:911.
[8] Noda I, Takahashi Y. Ber Bunsenges Phys. Chem 1996;100:696.