Colloid Polym Sci 275:284–287 (1997)

SHORT COMMUNICATION

V.A. Prevysh
B.-C. Wang
S.A. Khan
R.J. Spontak

Salting-in behavior of isotropic and anisotropic aqueous hydroxypropylcellulose solutions

Received: 4 June 1996
Accepted: 3 September 1996

V.A. Prevysh
Department of Pharmaceutical Chemistry
University of California
San Francisco, California 94143, USA

B.-C. Wang
Department of Materials Science
and Engineering
North Carolina State University
Raleigh, North Carolina 27695, USA

S.A. Khan
Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina 27695, USA

Prof. R.J. Spontak (✉)
Department of Materials Science
and Engineering
North Carolina State University
Raleigh, North Carolina 27695, USA

Abstract Salts with large polarizable ions are capable of *salting-in* complex aqueous polymer solutions exhibiting microstructure, thereby inducing changes in the phase behavior and properties of the solutions. In this work, the dynamic rheological properties of isotropic and mesomorphic hydroxypropylcellulose (HPC) in aqueous media have been investigated in the presence of one such salt, guanidine thiocyanate (GuSCN). Addition of this salt to isotropic aqueous HPC solutions is found to induce an increase in the magnitude of the elastic shear modulus (G'). At HPC concentrations above the isotropic → mesophase transition, however, addition of GuSCN results in a substantial reduction in G' due to microstructural changes in the chiral nematic HPC mesophase. This reduction in G' indicates that the microstructure of a water-soluble polymer exhibiting supramolecular organization can be tailored through salting-in, and is likewise expected to facilitate the commercial processing of HPC at high solids concentrations.

Key words Salting-in – hydroxypropylcellulose – rheology – chiral nematic mesophase – liquid crystal

Recent studies [1–5] have shown that the phase behavior and properties of complex aqueous polymer solutions (i.e., solutions exhibiting self-organized microstructure or assemblies) can be tailored through the addition of salts that promote *salting-in*. This phenomenon, well-established as a means to enhance the solubility and probe the conformational properties of biological macromolecules (e.g., proteins), occurs when salts with large, easily polarizable anions such as SCN^-, ClO_4^- and I^- (according to the Hoffmeister series [6]) inhibit hydrogen bonding between water molecules, thereby preventing the formation of transient water clusters [7, 8]. An increase in intermolecular interactions between water molecules and solvated macromolecules ensues, resulting in i) an increase in polymer solubility at constant temperature, and ii) an accompanying reduction in viscosity at constant polymer concentration. In recent studies, salting-in has been successfully utilized to increase the cloud point of alkyl polyglucosides [1], shift the gel envelope of poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) copolymers [2], reduce the viscosity of lignin-containing black liquor [3, 4] and tailor the degree of hydrogen-bonded interpolymer complexation [5].

Hydroxypropylcellulose (HPC), an important synthetic derivative of cellulose, is a semirigid macromolecule capable of exhibiting liquid crystallinity in a wide variety of solvents, including water. In particular, the phase behavior of aqueous HPC grades with molecular weights in the vicinity of 10^5 g/mol has been the focus of numerous studies [9–15], since these materials are commonly

utilized in commercial applications. While HPC solutions remain molecularly isotropic at ambient temperature and reasonably low polymer concentrations, HPC molecules self-organize into a chiral nematic (anisotropic) mesophase at higher concentrations (greater than *ca.* 40–43 wt%). Since such anisotropic solutions exhibit a well-described microstructure over a broad concentration range, they are ideally suited as model systems to probe the effect of salting-in [16, 17]. It has been recently found [16], for instance, that the solubility and chiral nematic pitch of anisotropic HPC both increase upon salting-in. In this work, the roles of salt and HPC concentration on the dynamic rheological properties of salted-in isotropic and anisotropic HPC solutions are examined.

The HPC grade examined here was Klucel-F with a molecular weight of about 10^5 g/mol, and the salt was guanidine thiocyanate ($NHC(NH_2)_2 \cdot HSCN$), designated GuSCN. This salt has been found [3, 5] to be very effective in salting-in aqueous polymer solutions exhibiting organized microstructure. Both materials were obtained from Aldrich and used as-received, without purification. Solutions were prepared by mixing HPC, GuSCN and distilled water to obtain predetermined polymer (Φ) and salt (ϕ) concentrations, and were allowed to equilibrate for 1 week. Here, Φ and ϕ denote weight fractions relative to the water content. A Rheometrics Mechanical Spectrometer (RMS 800) equipped with 25 mm parallel plates separated by a 1 mm gap was used to measure the stress response of the solutions to dynamic oscillatory shear strain $\gamma = \gamma_0 \sin \omega t$, where γ_0 denotes the strain amplitude, ω is the oscillatory frequency and t is time. The measured stress (τ) yielded the elastic (G') and viscous (G'') shear moduli from $\tau = G'\gamma_0 \sin \omega t + G''\gamma_0 \cos \omega t$ [18]. Variation in recorded measurements due to loading history [19] were eliminated by subjecting each sample to low-amplitude oscillatory shear, followed by 3 min of quiescent recovery, prior to analysis.

Figures 1 and 2 illustrate the dependence of the elastic and viscous moduli on strain (γ) and frequency (ω), respectively, for anisotropic HPC solutions at two different salt concentrations (ϕ). In the case of the virgin solution with no added GuSCN, G' exceeds, and is nearly parallel to, G'' at low γ (see Fig. 1), indicating the presence of a network-like structure (possibly due to the HPC mesophase). Within this regime, linear viscoelasticity (LVE) is also observed, since G' and G'' are virtually independent of γ. With increasing strain, G' and G'' converge until they cross. Such G'–G'' crossover reveals substantial collapse of existing microstructure or deformation of a defect network [20]. Upon addition of salt ($\phi = 0.20$), however, G'' exceeds G' over the entire strain range, revealing that the HPC molecules in this solution are not as rigidly ordered as those in the virgin solution. Comparable results are evident in the corresponding frequency sweeps, performed at $\gamma = 10\%$

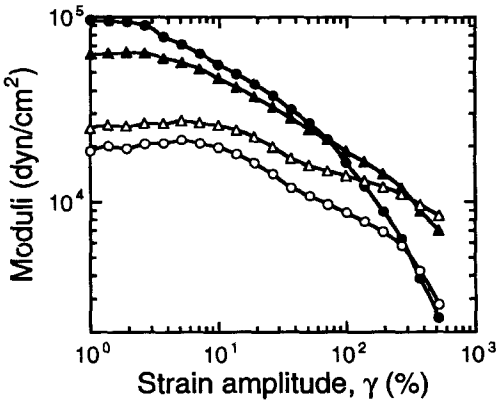

Fig. 1 Variation of the dynamic elastic (G', circles) and viscous (G'', triangles) moduli with strain for a chiral nematic HPC solution ($\Phi = 0.56$) at two GuSCN concentrations (ϕ): 0.00 (filled) and 0.20 (open). Experiments were conducted at a frequency (ω) of 10 rad/s

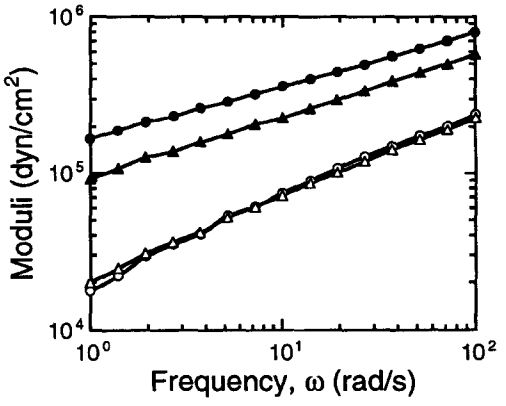

Fig. 2 Double-logarithmic representation showing the ω-dependent dynamic shear moduli for an anisotropic HPC solution ($\Phi = 0.60$) at two salt concentrations (ϕ). The symbols are the same as those listed in the caption of Fig. 1. Experiments were conducted at a strain amplitude (γ) of 10%

and displayed in Fig. 2. While G' exceeds G'' over two decades of frequency in the same unsalted solution shown in Fig. 1, G' and G'' are almost indistinguishable when $\phi = 0.20$. Since GuSCN is expected to enhance HPC–H_2O interactions and decrease the hydrophobicity of HPC [5], a decrease in the extent of supramolecular order appears to be accompanied by a reduction in G'.

The behavior seen in Figs. 1 and 2 is consistent with recent evidence suggesting that the morphology of the HPC mesophase is altered, appearing less distinct [17] and increasing in pitch [16], upon addition of any of several SCN^- salts. Figure 3 shows the effect of salt concentration (ϕ) on four HPC solutions, two isotropic and two anisotropic. In this figure, we have normalized the

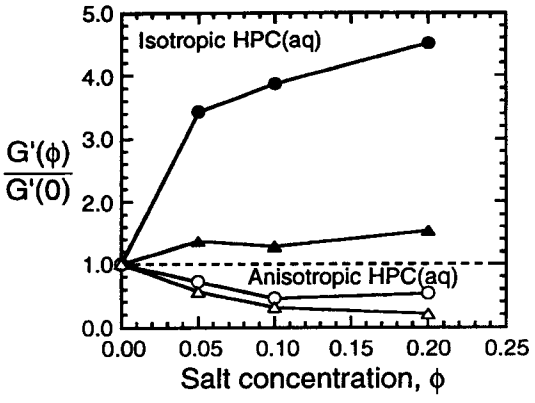

Fig. 3 Normalized $G'(\phi)$, relative to G' of the corresponding virgin (unsalted) solution, for four HPC concentrations (Φ): 0.20 (●), 0.33 (▲), 0.43 (○) and 0.55 (△)

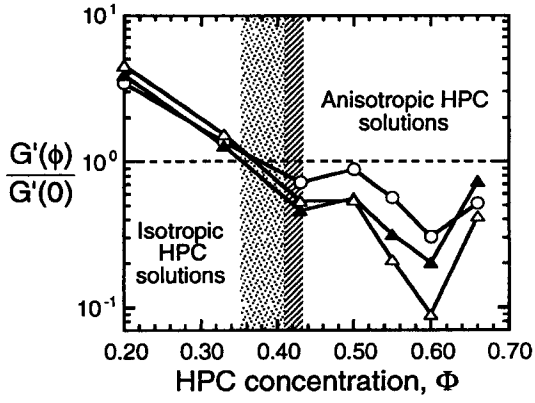

Fig. 4 Variation of $G'(\phi)/G'(0)$ with Φ for three GuSCN concentrations (ϕ): 0.05 (○), 0.10 (▲) and 0.20 (△). The cross-hatched region denotes the expected I → M transition range [9–15], and the shaded region shows where localized supramolecular ordering first occurs [21, 22]

elastic modulus $G'(\phi)$ from each salt-containing HPC solution (measured from the LVE regime of a strain sweep) with respect to that from the corresponding parent solution without GuSCN. It is evident from Fig. 3 that addition of GuSCN to anisotropic HPC solutions serves to decrease G', in some cases by more than an order of magnitude. In contrast, GuSCN has the opposite effect (it increases G') in isotropic solutions. Since no corroborative data are presently available to explain the relative increase in G' reported here for salted-in isotropic HPC solutions, additional work is clearly needed to resolve this issue.

The variation in $G'(\phi)/G'(0)$ with HPC concentration for salt concentrations ranging from 0.05 to 0.20 is more clearly evident in Fig. 4. According to the data shown in this figure for isotropic HPC solutions, $G'(\phi)/G'(0)$ is observed to exceed unity (as in Fig. 3) and decrease with increasing Φ. Note that, within this isotropic regime, $G'(\phi)/G'(0)$ is nearly independent of salt concentration. The HPC concentrations corresponding to $G'(\phi)/G'(0) = 1$ for the data sets shown in Fig. 4 fall in the concentration range wherein localized supramolecular ordering is first observed at ambient temperature [21, 22]. At higher HPC concentrations, near the isotropic → mesophase (I → M) transition, $G'(\phi)/G'(0)$ exhibits a local minimum before reaching a global minimum within the HPC mesophase, in the vicinity of $\Phi \approx 0.6$. The depth of this global minimum appears to increase with salt concentration. From these and other [3, 4] data, it can be concluded that the efficacy of salting-in polymer microstructure in aqueous media is more pronounced at high solids concentrations.

In this work, we have demonstrated that salting-in can be used as an alternative means by which to modify the microstructure, and consequently tailor the rheological properties, of isotropic and anisotropic HPC aqueous solutions. For complex polymer solutions exhibiting extensive supramolecular organization in a mesophase (e.g., anisotropic aqueous HPC), addition of GuSCN results in both a reduction in the elastic modulus and molecular restructuring of the mesophase. As in other polymer solutions exhibiting microstructure [3–5], salting-in is found to be most effective at high HPC concentrations. In the case of salted-in isotropic HPC solutions, however, the presence of GuSCN induces an anomalous increase in solution elasticity relative to the unsalted parent solutions. From this and related studies, salting-in constitutes an intriguing, and apparently underutilized, method of probing colloidal interactions in complex aqueous polymer solutions exhibiting microstructure, as well as controlling macroscopic properties of practical interest in commercial processing.

Acknowledgments This work was supported by the TAPPI Foundation.

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