Polymer Bulletin 49, 281–288 (2002)

Polymer Bulletin

Dynamics in aqueous solutions of poly(vinyl alcohol) and its hydrophobically modified anionic analogues

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Received: 19 July 2002/Revised version: 10 October 2002/ Accepted: 10 October 2002

Summary

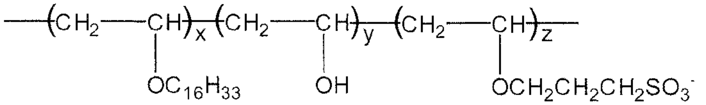
The dynamics of aqueous solutions of unmodified poly(vinyl alcohol) (PVA) and of hydrophobically modified anionic analogues with two different degrees of hydrophobic substitution (HMPVA1 and HMPVA2) is studied with the aid of viscometry and dynamic light scattering (DLS). The viscosity results reveal a pronounced polyelectrolyte effect in dilute solutions of HMPVA1, while strong association effects, even at very low concentrations, are observed in solutions of the analogue with the highest hydrophobicity. The relaxation times for solutions of PVA are practically independent of concentration over the considered range. For the hydrophobically modified analogues, both the fast and the slow relaxation times increase with increasing concentration for both systems, but the concentration dependencies of the relaxation times are much stronger for HMPVA2 due to enhanced hydrophobic associations.

Introduction

Amphiphilic polymers that spontaneously form supramolecular structures in aqueous media mainly due to hydrophobic interactions have attracted a great deal of interest in recent years [1-7]. Hydrophobically modified polyelectrolytes are such systems that belong to this class of self-associating polymers. In these systems, hydrophobic associations can take place through intra- or interpolymer interactions competing with electrostatic repulsions, which operate within the same polymer chain or between different chains. The preference of intra- or interpolymer hydrophobe association depends on the polymer concentration and the structural characteristics of the macromolecule, notably the content and the nature of the hydrophobic groups and the sequence distribution of electrolyte and hydrophobic monomer units along the polymer chain. These effects and the ionic strength of the system are factors that also are important [8,9] for the association efficiency and subsequently the dynamical behavior of solutions of hydrophobically modified polyelectrolytes. Numerous theoretical studies [10-19] in recent years have been devoted to properties of polyelectrolyte solutions.

The solution behavior of linear polyelectrolytes has been investigated extensively by light scattering [20-34] in order to survey long-range interchain dynamics of polyions.

The appearance of a fast and a slow diffusive mode in the correlation function from dynamic light scattering (DLS) of linear polyelectrolytes in dilute to semidilute aqueous solutions in the low-salt limit has attracted a great deal of interest in recent years and several models have been developed to explain this phenomenon [22,23,35,36]. The slow diffusive polyelectrolyte mode has been detected in a wide variety of synthetic and biological polymers in solutions of low ionic strength [22,36-40]. The fast mode is usually interpreted as arising from coupled diffusion of polyions and low-molecular-weight counterions, while the slow mode has been attributed to the existence of supramolecular structures or large-scale heterogeneities in solution. Although the properties of these systems are governed mainly by the interplay between the strong attraction between hydrophobic groups (stickers) and the repulsion originated from the charges located on the polymer chains and the mobile counterions, it is unclear to what extent hydrophobic modification of polyelectrolytes influences the overall dynamical features. The principal objective of the present work is to elucidate how the competition between electrostatic and hydrophobic interactions influences the dynamics of hydrophobic polyelectrolyte systems.



$$-(CH_2-\underset{OC_{16}H_{33}}{CH})_x-(CH_2-\underset{OH}{CH})_y-(CH_2-\underset{OCH_2CH_2CH_2SO_3^-}{CH})_z-$$

HMPVA1: $x = 0.011$ $z = 0.026$
HMPVA2: $x = 0.020$ $z = 0.026$
$y = 1 - x - z$

Figure 1. Schematic picture of the hydrophobically modified poly(vinyl alcohol) with anionic functionality

With this intention in mind, we have conducted dynamic light scattering on aqueous solutions of the nonionic precursor polymer poly (vinyl alcohol) (PVA) and two hydrophobically modified analogues (with different amounts of hydrophobic groups) with the same anionic functionality (see Figure 1). In this paper, our attention is focused on the dynamical properties of the systems. Since capillary viscometry is a powerful technique to characterize polyelectrolyte effects, some viscosity measurements were carried out on aqueous solutions of the hydrophobically modified polyelectrolytes to elucidate the interplay between electrostatic and hydrophobic interactions. The incorporation of hydrophobic groups reduces the water-solubility of the polymer, while the ionic groups counteract this effect. By changing the polymer concentration and the hydrophobicity of the polymer, we can tune the strength of the polyelectrolyte effect and the inclination of the system to form association complexes. In this way, we hope to gain some insight into the intricate interplay between electrostatic and hydrophobic interactions. In a recent pulsed field gradient NMR study [42] of these systems, the polymer self-diffusion results revealed a complex picture of the competition between the repulsive Coulombic forces and the associations induced by the hydrophobic interactions.

Experimental

Materials and Sample Preparation

The PVA precursor was purchased from TCI-EP and its weight-average molecular weight are 108 000, and the polydispersity index is 1.4. The polymer was further hydrolyzed and the final degree of saponification was very close to 100 mol %. The two hydrophobically modified polymers contain the same amount (2.6 %) of ionic sulfonate groups, while the number of hydrophobic hexadecyl groups randomly substituted on the alcohol groups of the parent molecules is different. The polymer designated HMPVA1 contains 1.1 % hydrophobic groups, while the other sample denoted HMPVA2 carries 2.0 % hexadecyl groups. These hydrophobic polyelectrolytes were synthesized according to a procedure described elsewhere [41]. Some details on characterization and sample preparation are reported previously [41,42]. All the experiments were carried out at 25 °C.

Capillary Viscometry

Viscosity measurements were performed with a standard Ubbelohde viscometer, with solvent flow times larger than 180 s, placed into a temperature-controlled water bath at 25 ± 0.05 °C. The solutions were filtered to remove dust and other traces of impurities.

Dynamic Light Scattering Experiments

Dynamic light scattering measurements were performed with a laboratory made light scattering goniometer, using an argon ion laser (Spectra Physics model 2020) operating at 514.5 nm with vertically polarized light as the light source. The measurement temperature was controlled at 25.00 ± 0.05 °C. The sample solutions were filtered in an atmosphere of filtered air through 0.8-5 μm (depending on the viscosity of the solutions) filters (Millipore) directly into precleaned 10- or 16-mm NMR tubes, depending on the concentration. However, for solutions of the hydrophobically modified analogues, especially at higher concentrations, filtration was not possible but the samples were cleaned by centrifugation (2000 r.p.m.) for several hours. The correlation functions obtained from solutions where both procedures can be used were identical. We have not detected any significant difference between samples that have been centrifuged or filtered.

The scattering process allows us to explore a system on a length scale of q^{-1}, where q is the wave vector defined as $q = 4\pi n \sin(\theta/2)/\lambda$. Here λ is the wavelength of the incident light in a vacuum, θ is the scattering angle and n is the refractive index of the solution. The value of n was determined at each concentration for the different polymers at $\lambda = 514.5$ nm by using an Abbé refractometer.

Analysis of the Dynamic Light Scattering Data

If the scattered light obeys Gaussian statistics, the experimentally determined homodyne intensity autocorrelation function $g^{(2)}(q,t)$ is directly related to the theoretically amenable first-order electric field autocorrelation function $g^{(1)}(q,t)$, through the Siegert expression $g^{(2)}(q,t) = 1 + B|g(1)(q,t)|^2$, where B ($\leq 1$) is an instrumental parameter.

Several previous investigations [43-46] on associating and gelling polymer systems have shown that the decay of the correlation function can be described by a single exponential, followed at longer times by a stretched exponential. In the present work we have utilized a more general expression, consisting of a double stretched exponential function, to describe the decay of the correlation functions [47]

$$g^{(1)}(t) = A_f \exp[-(t/\tau_{fe})^{\alpha}] + A_s \exp[-(t/\tau_{se})^{\beta}] \qquad (1)$$

with $A_f + A_s = 1$. The parameters A_f and A_s are the amplitudes for the fast and the slow relaxation modes, respectively. The variables τ_{fe} and τ_{se} are some effective relaxation times, and α ($0 < \alpha \leq 1$) and β ($0 < \beta \leq 1$) measure the widths of the distribution of relaxation times. The mean relaxation times are given by $\tau_f = (\tau_{fe}/\alpha)\Gamma(1/\alpha)$, $\tau_s = (\tau_{se}/\beta)\Gamma(1/\beta)$ where Γ is the gamma function.

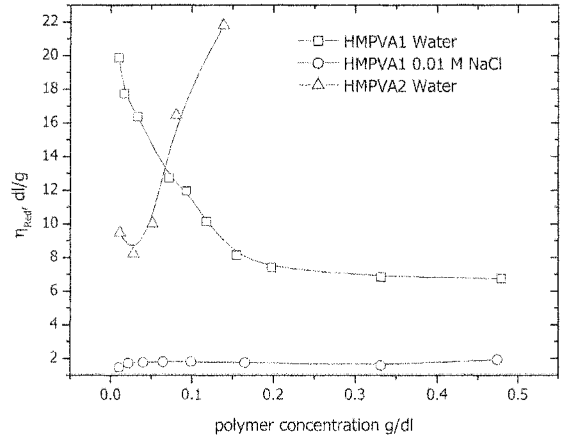


Figure 2. The reduced viscosity as a function of polymer concentration for the systems indicated. The error in the data is of the same size as the data points.

A nonlinear fitting algorithm (a modified Levenberg-Marquardt method) was employed in the analysis of the correlation functions to obtain best-fit values of the parameters appearing on the right-hand side of Equation (1). For all the solutions of PVA, the correlation functions are well described by a single stretched exponential (the first term on the right-hand side of Equation (1)), while the correlation functions for the hydrophobically modified samples always exhibit two relaxation modes and are well portrayed by Equation (1). For the solutions of HMPVA1, the values of α are virtually identical to 1 (a single exponential behavior), while for the more associating HMPVA2 samples somewhat lower values of α are observed. The value of β generally decreases with increasing concentration, starting from around 0.8 at the lowest polymer concentrations and ending around 0.5 for the highest polymer concentrations.

Results and discussion

Viscometry

The results of viscometric measurements are presented in the form of reduced viscosity versus concentration. Figure 2 contains the data obtained for the two hydrophobically modified samples (HMPVA1 and HMPVA2) in water and for solutions of the least hydrophobically modified polymer (HMPVA1) in the presence of salt. The data for HMPVA1 in water exhibits an upturn in reduced viscosity at low concentrations, representative of polyelectrolyte behavior. In the case of the polymer (HMPVA2) with the highest hydrophobicity, there is a tendency of a polyelectrolyte effect at very low polymer concentrations. The strong increase of the reduced viscosity at higher concentrations can probably be attributed to the progressive dominance of the hydrophobic association effects. This finding suggests that the hydrophobic effect plays an important role already at fairly low concentrations for the HMPVA2 sample.

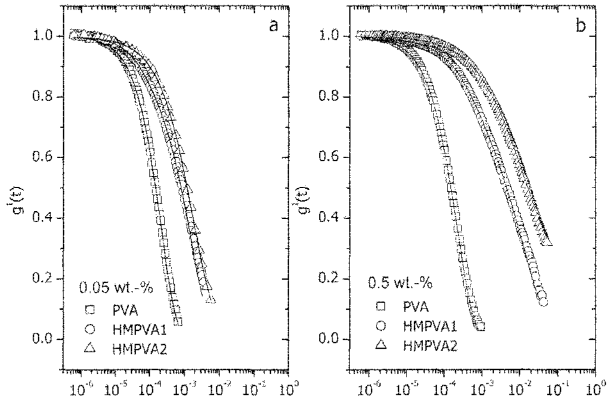


Figure 3. Plot of the first-order electric field correlation function versus time (every third data point is shown) at a scattering angle of 60° for the samples and concentrations indicated. The solid curves are fitted with the aid of Equation (1) (See the discussion below for details).

By addition of salt to the solutions of HMPVA1, the reduced viscosity falls off significantly and is virtually independent of polymer concentration. This result indicates that the electrostatic interactions are screened and the molecules contract.

Dynamic light scattering

The effect of hydrophobicity on the time correlation functions, at a fixed scattering angle of 60°, is depicted in Figure 3, at two different polymer concentrations. The solid curves are fitted with the aid of Equation (1), taking into account the modifications discussed above. It is evident that the decay time is shifted toward higher values when the degree of hydrophobic substitution is raised from 0 (PVA) to 2.1 (HMPVA2) mol %, and this slowing down effect is enhanced with increasing polymer concentration. This observation further indicates that the hydrophobic effect becomes more prominent as the polymer concentration increases.

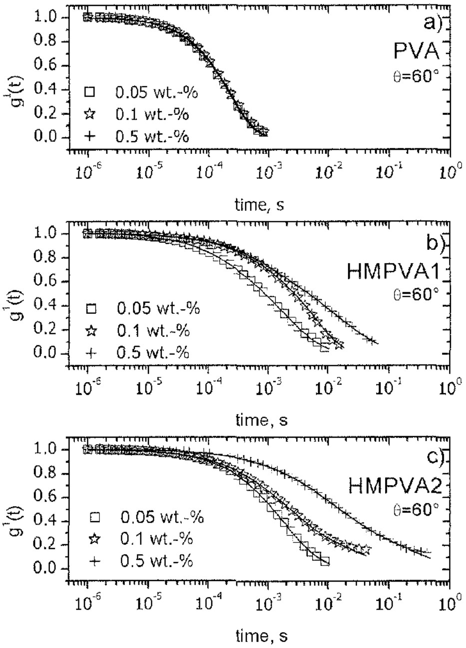


Figure 4. Plot of the first-order electric field correlation function versus time (every third data point is shown) at a scattering angle of 60° for the systems and concentrations indicated. The solid curves are fitted with the aid of Equation 1. (See the discussion below for details.)

The influence of polymer concentration on the decay of the relaxation function for the three polymer systems is illustrated in Figure 4. The effect of concentration is absent in the case of PVA, while for the HMPVA1 and HMPVA2 samples a pronounced slowing down of the long-time relaxation process is observed as the concentration increases. This effect is more pronounced for the HMPVA2 sample and is another manifestation of the impact of the hydrophobic effect at higher concentrations. The moderate effect observed for HMPVA1 at low concentration, probably reflects that the tendency to form association complexes is suppressed by the electrostatic repulsive forces.

Figure 5 shows the concentration dependences of the relaxation times, calculated with the aid of Equation (1), at a fixed scattering angle (the same trend is observed at all scattering angles). The fast relaxation time τ_f exhibits virtually no concentration dependence for the PVA-water system (see Figure 5a) and the values of τ_f at higher concentrations are lower than for the other systems. A weak concentration dependence of τ_f has previously been reported [47] for aqueous solutions of PVA. We may note that the concentration dependency of τ_f becomes stronger as the hydrophobicity of the

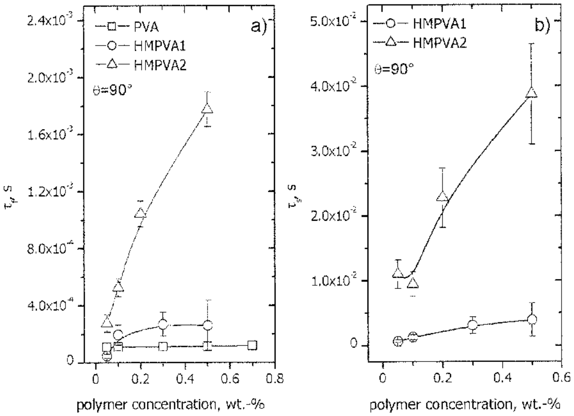


Figure 5. Concentration dependence of the fast (τ_f) (a) and slow (τ_s) (b) relaxation time at a scattering angle of 90° for the polymer samples indicated. The error bars for the PVA solutions are of the same magnitude as the symbol size.

polymer increases. This trend can probably be attributed to an enhanced tendency for the hydrophobically modified samples to form association complexes at higher concentrations, and thereby the dynamics is slowed down. The moderate concentration dependence of τ_f for HMPVA1 reflects the intricate interplay between electrostatic and hydrophobic interactions.

The concentration dependence of the slow relaxation time τ_s is similar as that of the fast relaxation time for the hydrophobic systems (see Figure 5b).

Acknowledgements.

Rolf A. Lauten wishes to thank the Norwegian Research Council for financial support.

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