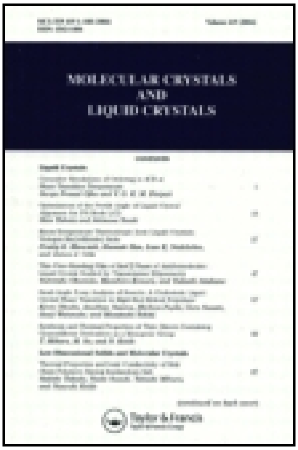

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The Effect of Temperature on the Self-Assembly of Deoxyguanosine 5′-Monophosphate in Pretransitional Region of the I-Ch Phase Transition

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THE EFFECT OF TEMPERATURE ON THE SELF-ASSEMBLY OF DEOXYGUANOSINE 5′-MONOPHOSPHATE IN PRETRANSITIONAL REGION OF THE I-CH PHASE TRANSITION

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Temperature dependence of the self-assembly of deoxyguanosine 5′-monophosphate in pretransitional region of the I-Ch phase transition was investigated by dynamic light scattering. Measurements reveal the presence of two diffusive modes: the slower mode is attributed to the motion of large globular aggregates, while the faster mode is related to the translational motion of the self-assembled columnar stacks. By increasing temperature the number of assembled molecules decreases, as seen from a reduction in the fast mode amplitude, until this mode finally disappears. Dynamical behavior of the slow diffusive mode is more complex and coupled to the dynamics of the fast mode.

Keywords: lyotropic liquid crystals; polyelectrolytes; self-assembly

INTRODUCTION

self-assembling systems are an interesting subject of investigation due to their many degrees of freedom. One of the most studied molecules that

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forms complex self-assembled structures is guanosine. The basic aggregation unit is a planar tetramer (Fig. 1(a)) formed by four guanosine molecules [1]. The vertical stacking of these tetramers induces the formation of long columnar stacks (Fig. 1(b)), which in congested solutions exhibit lyotropic liquid crystalline polymorphism forming the cholesteric and hexagonal phases [2].

The stacking process and column growth start already quite below the I-Ch phase transition. Our recent investigations [3,4] of deoxyguanosine 5′-monophosphate by dynamic light scattering show that this pretransitional region is characteriezed by the appearance of a fast diffusive process, which is attributed to the translational motion of the columnar stacks. The concentration dependence of this diffusive process has been already studied in detail [4]. Lyotropic systems, however, are characterized by solution concentration as well as temperature. Therefore, we aim our present work to the investigation of temperature dependence of the self-assembling process in pretransitional region of the I-Ch phase transition.

EXPERIMENT

Deoxyguanosine 5′-monophosphate (d(pG)) was purchased from Sigma (St. Louis, USA; 99% purity) in the form of sodium salt. The ammonium salt d(pG) was obtained by an ion exchange procedure followed by subsequent lyophilization. We prepared an isotropic $c = 5$ wt% solution by mixing the lyophilized material with distilled water and analyzed it after an equilibration time of 24 hours.

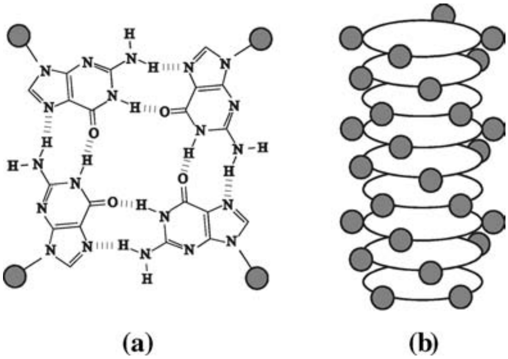


FIGURE 1 Microscopic scheme of the self-assembly process of guanosine molecules. (a) The formation of the tetramer. The gray spheres indicate the sugar-Phosphate groups. (b) Vertical stacking of the tetramers.

We studied the dynamics of the d(pG) solution by dynamic light scattering (DLS), the experimental setup being in detail described elsewhere [4]. The light source was a He-Ne laser with the wavelength of $\lambda = 632.8\,\mathrm{nm}$. The intensity correlation function was measured using an ALV5000 digital correlator (ALV-Laser Vertriebgesellschaft, Langen, Germany). The normalized intensity correlation function $g_2(t) = \langle I(0)I(t)\rangle / \langle I\rangle^2$ of light scattered on the sample was measured as a function of temperature at a fixed scattering angle ($\vartheta = 50°$). In our scattering geometry the polarizations of the incident and scattered light were selected to be parallel (polarized scattering). The investigated solution was introduced into a capillary tube that was immersed in a specially constructed index-matching bath with a heater. The temperature of the bath and the sample was regulated with a temperature controller (Oxford ITC4) to within ± 0.1°C. The temperature range investigated ranged from 22°C to 72°C.

The measured intensity correlation function probes the dynamical response of the system. which can be written as [5,6]

$$g_2(t) = 1 + \left| \sum_i A_i \exp(-t/\tau_i)^{\beta_i} \right|^2 . \tag{1}$$

A_i is the amplitude of the i-th relaxation mode and the corresponding average relaxation time is given by $\langle \tau_i \rangle = \tau_i \Gamma\left(\beta_i^{-1}\right)/\beta_i$, where $\Gamma\left(\beta_i^{-1}\right)$ is the gamma-function. The parameter β_i is a measure of the width of the distribution of relaxation times (polydispersity). Very narrow distributions correspond to $\beta_i \sim 1$, while smaller values of β_i indicate broader distributions. From the average relaxation times the translational diffusion coefficients were calculated as

$$D_i = \frac{1}{\langle \tau_i \rangle q^2} \tag{2}$$

where q is the scattering vector given as $q = (4\pi n/\lambda)\sin(\vartheta/2)$ and $n = 1.33$ is the solution refractive index.

At room temperature two relaxation mode ($i = 2$) appear in the intensity correlation function (Fig. 2). The faster mode is related to the dynamics of the d(pG) columnar stacks, while the slower mode is assigned to the translational motion of large globular aggregates [4]. The increase of the temperature induces a gradual decrease of the amplitude of the fast DLS mode until it actually disappears at $T = 28°\mathrm{C}$. In the temperature range $22°\mathrm{C} < T < 28°\mathrm{C}$ the diffusion coefficient of the fast mode, D_f, decreases nearly linear with temperature (Fig. 3(a)). The parameter β_f has in this temperature range an approximately constant value of $\beta_f = 0.92 \pm 0.05$ indicating scattering from nearly monodisperse objects.

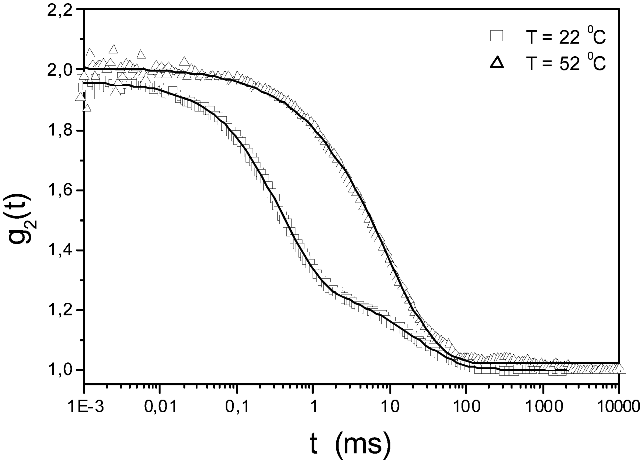
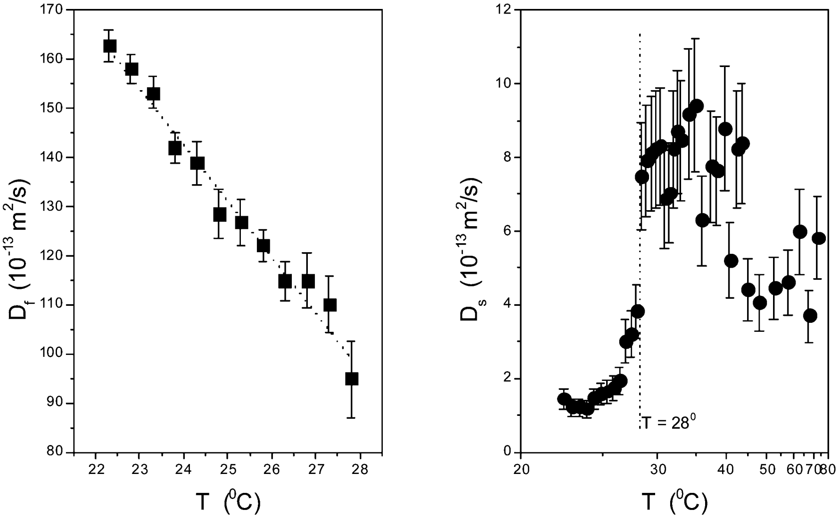


FIGURE 2 Intensity correlation functions for a $c = 5$ wt% ammonium d(pG) solution. Solid lines are fits to Eq. (1).



(a) **(b)**

FIGURE 3 Temperature dependence of the diffusion coefficients of the fast (a) and the slow relaxation mode (b).

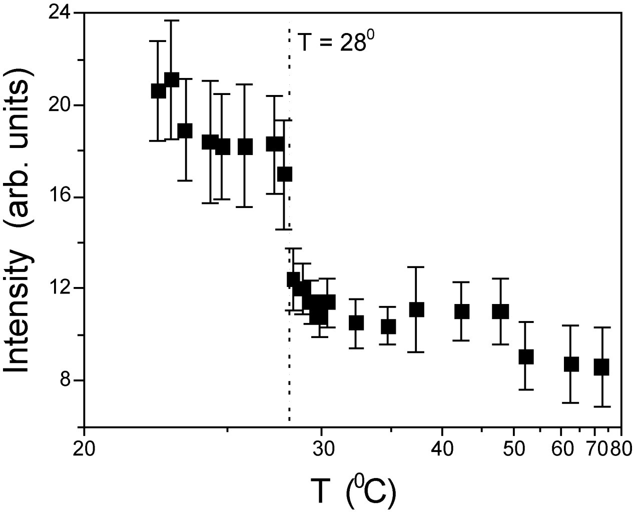


FIGURE 4 The temperature dependence of the integral intensity of the scattered light.

The slow mode, on the other hand, is present in the whole temperature range investigated. At room temperatures the value of the slow diffusion coefficient remains roughly constant. $D_S = 1.5 \pm 0.3 \cdot 10^{-13} \mathrm{m}^2/\mathrm{s}$ (Fig. 3(b)). The disappearance of the fast mode at $T = 28°\mathrm{C}$, interestingly, coincides with a jump of the D_S value. At higher temperatures the values of D_S are quite scattered, but some slowing down can still be resolved. Although the values of the parameter β_S are very scattered, at room temperature an average value of $\beta_S = 0.64 \pm 0.06$ is obtained. This value steeply increases to $\beta_S = 0.80 \pm 0.04$ at $T > 28°\mathrm{C}$ but gets again reduced at high temperature (data not shown). To gain more information on the coupled behavior of the two modes also the total intensity of the scattered light has been investigated. The disappearance of the fast mode is observed as a drop in the scattering intensity indicating that the number of the scattering objects was reduced (Fig. 4).

DISCUSSION

The fast DLS mode shows a slowing down with increasing the temperature. At the same time its amplitude is reduced, which indicates that the number of the d(pG) stacks in the solution is decreasing. Similar behavior is observed when the d(pG) concentration is lowered at a fixed temperature [4]. The fact that the fast mode disappears already at 28°C can be attributed to the low number of assembled molecules at the $c = 5$ wt% concentration. Previous ^{31}P NMR measurements revealed that at $T = 25°C$ only 13.6% of the molecules are involved into the formation of columnar stacks [4]. Temperature dependent "melting" behavior of guanosine stacks has been also observed by other experimental methods, for example NMR spectroscopy [7–9], interferometric DLS [10], X-ray and circular dichroism spectroscopy [11–14], and is in agreement with out observations.

Interesting is the temperature dependence of the slow DLS mode. Investigation by freeze fracture electron microscopy revealed that this mode is very probably related to the translational motion of globular aggregates of about 100 mm in diameter [4]. From the electron micrographs, however, no information on the inner structure of the globules could be obtained. But as the slow mode is observed also in sodium salt d(pG), which shows a much weaker self-assembly than the ammonium salt [4], we propose that the globular aggregates are formed of monomers or tetramers rather than the d(pG) columnar stacks. In general, the presence of a slow DLS mode is a typical property of various polyelectrolyte systems including the DNA [15–19]. This mode is usually interpreted as arising from temporal aggregates, but there is still much speculation on forces that induce their formation [15,17,20,21]. Although much work was done on investigating the effect of polyion concentration and the effect of added ions, only little data is available on the temperature behavior of this mode.

Our measurements show that the temperature behavior of the slow DLS mode in guanosine solutions is rather complex and coupled to the appearance [4] and disappearance (Fig. 3(b)) of the fast DLS mode. EM micrographs show that single globular aggregates have a uniform size distribution, but also have tendency towards clustering. This explains the broad relaxation times distribution given by $\beta_s = 0.64$ and arising from different average cluster dimensions. When the fast mode disappears at $T = 28°C$, the D_s value increases more than 4 times. This can be interpreted as a reduction in the average cluster size and the d(pG) stacks, therefore, act as a "glue" that holds the globular aggregates together. The globular aggregates also seem to be thermodynamically stable since at higher temperatures their number decreases only slightly (Fig. 4).

CONCLUSION

The temperature dependence of a $c = 5$ wt% d(pG) solution investigated by DLS shows some interesting features. The behavior of the fast DLS mode with increasing temperature resembles the behavior observed when the d(pG) concentration is lowered at a fixed temperature. This indicates that the number of assembled d(pG) molecules is reduced, which is in agreement with previous studies by other techniques [7–14]. The disappearance of the fast mode, however, has an enormous effect on the dynamics of the slow DLS mode, resulting in a large jump in the value of its diffusion coefficient. This shows that the dynamics of the d(pG) stacks is coupled to the motion of the globular aggregates.

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