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Structure and Viscoelasticity of Interacting Spherical Brushes

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SUMMARY: Star polymers with a high functionality of 128 are viewed as ideal spherical brushes with soft colloidal character, encompassing both polymer-like short range and colloid-like long range interactions. We have identified three mechanisms for relaxing the concentration and density fluctuations in semidilute solution: cooperative diffusion, characteristic of polymers, and self-diffusion and structural relaxation, characteristics of colloidal hard spheres. Upon heating these systems undergo a reversible liquid-solid transition, yielding weak gels. It is attributed to the trapping of the spheres in "cages" due to the swelling with temperature and hence stronger arm interpenetration. At the transition strong hysteresis phenomena are observed during steady and transient shear measurements, and relate to the changing viscoelastic character of the fluid with temperature.

Introduction

The synthesis multiarm star polymers$^{1)}$ has opened the route to the exploration of the dynamics of ultrasoft mesoscopic systems. Due to their inherent monomer density heterogeneity, yielding a core-shell structure, these systems exhibit liquid-like order in concentrated solutions, as a result of the interplay between the osmotic pressure and the arm entropic stretching$^{2,3)}$. Using dynamic light scattering, and with the aid of a mean-field theoretical approach, we have identified the various mechanisms contributing to the relaxation of concentration and density fluctuations in semidilute solutions of such polymers$^{2,4)}$. They reveal their dual polymeric-colloidal character, and are: cooperative diffusion (polymeric origin); and self diffusion (functionality polydispersity) and

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structural relaxation, both of colloidal origin[5)]. Using this knowledge, we investigate the effects of temperature on the structure and dynamics of concentrated solutions of such hyperstars in good solvent. In such situations, these polymers are already organized in a soft liquid order and we explore their viscoelastic properties as function of temperature.

Experimental

This work focuses on the investigation of a high functionality 1,4-polybutadiene star (f=128 arms) with nominal molecular weight per arm M=28000, nearly monodisperse. Solutions in the good solvent decane were obtained (because of its large refractive index contrast to polybutadiene and high boiling point for eliminating evaporation problems) in a range of concentrations, from 7.9% wt (c/c^*=9.9) to 9.5 % wt (c/c^*=12). A limited number of dilute solutions (up to 1% wt) were also utilized for characterization purposes. The dynamics of these solutions was investigated in a temperature range from 5 to 55 °C using shear rheology in both the linear and nonlinear regimes, as well as dynamic light scattering.

Results and Discussion

Dynamic light scattering measurements in dilute solution (single ultrasoft spheres) reveal a positive second virial coefficient which increases slightly with temperature. At higher concentrations ($c>c^*$), the light scattering spectrum reveals the presence of cooperative and self diffusion processes[2,4)]. Concerning the former, it is interesting that, whereas the temperature dependence of its relaxation rate follows that of the solvent viscosity, as expected (and it becomes faster as the concentration is further increased), its intensity drops with temperature, signifying enhanced interpenetration. On the other hand, the self diffusive mode slows down (unexpectedly) and looses intensity as the temperature increases[6)].

The effects of temperature on the dynamics of this system are also manifested in its linear viscoelastic properties obtained from small amplitude oscillatory shear measurements, as illustrated in Fig. 1. At relatively low temperatures ($T\leq20$°C) the star solution (7.9% wt) behaves as an ordinary liquid with typical Rouse-like terminal relaxation. However, as the temperature increases to 55°C, the material behavior changes drastically to solid-like response with nearly frequency-independent storage and loss moduli. It is noted that this effect is entirely reversible. Further, the observed increase in moduli through this transition (more than two orders of magnitude) is much higher than the respective slowing down of the self diffusion (nearly factor of 3). Preliminary results from a structural analysis of the weak solids using SANS suggest that at high temperatures a gel is formed, and thus the phenomenon is attributed to a reversible thermal gelation$^{6)}$.

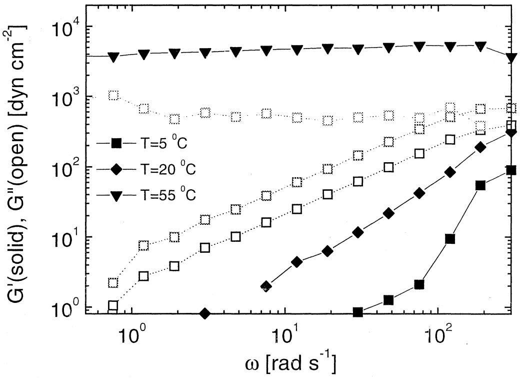

Fig. 1: Dynamic frequency sweep tests in the linear viscoelastic regime for a hyperstar solution (f=128 and M=28000, 7.9% wt) in decane, at various temperatures, indicating the storage (G') and loss (G'') moduli.

From the compilation of the above results, the emerging picture of the effects of heating on the structure and dynamics of these hyperstar polymer solutions suggests that as the temperature increases and the solvent quality improves, the hyperstars swell, and a stronger arm interpenetration takes place, yielding eventually a trapping of the cores and thus a weak solid response. This is consistent with information on the long-time diffusion obtained from pulsed field gradient NMR data as well^6.

This transition is further characterized by an unusual viscoelastic response in steady shear experiments. In particular, as seen in Fig. 2, at low temperatures in the 'liquid-like behavior' region (6 °C), when we raise gradually the shear rate and then immediately decrease it in an identical manner back to zero, the shear stress response is nearly Newtonian fully reversible. On the other hand, at high temperatures in the 'solid-like behavior' region (12 °C), a strong hysteresis effect is observed along with a non-monotonic response accompanied by a yield stress (which increases with temperature); the latter behavior is characterized by three shear rate regimes: linear elastic response at low shear rates, viscous flow (structural break down) at high shear rates, and nonlinear viscoplastic behavior at intermediate shear rates. These phenomena are related to the shear-induced structural changes and depend on the distance from the transition temperature as well as the molecular characteristics of the stars[6]. They can be in principle rationalized by considering semi-phenomenological models of thixotropy considering the interplay of the viscous and elastic contributions (which are interrelated through the cohesiveness of the structure) to the overall stress response[7].

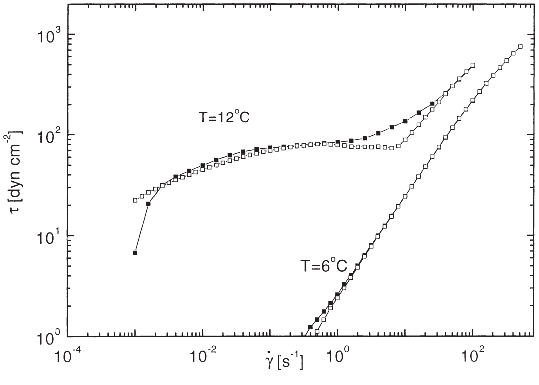

Fig. 2: Steady stress sweeps for the multiarm star solution (f=128 and M=28000, 9.5% wt) in decane, at two temperatures. Solid symbols: increasing shear rate; open symbols: decreasing shear rate.

Conclusions

Multiarm star polymers exhibit a reach dynamic response because of their inherent topological heterogeneity and can be considered as model ultrasoft spheres, encompassing both polymeric and colloidal properties, and having several similarities with, and distinct differences from block copolymer micelles8,9,10). In semidilute solution they display cooperative diffusion, characteristic of polymers relaxing the concentration fluctuations, and self-diffusion and structural relaxation, characteristics of colloidal hard spheres relaxing the density fluctuations. Upon heating these systems undergo a reversible gelation transition, which is characterized by strong hysteresis phenomena because of the changing viscoelastic character of the fluid with temperature.

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