Available online at www.sciencedirect.com
ScienceDirect
Colloids and Surfaces A: Physicochem. Eng. Aspects 316 (2008) 159–170
COLLOIDS AND SURFACES A
www.elsevier.com/locate/colsurfa

Anomalous turbidity, dynamical, and rheological properties in aqueous mixtures of a thermoresponsive PVCL-g-$C_{11}EO_{42}$ copolymer and an anionic surfactant

Anna-Lena Kjøniksen [a], Antti Laukkanen [b],
Heikki Tenhu [b], Bo Nyström [a,*]

[a] Department of Chemistry, University of Oslo, P.O. Box 1033, N-0315 Oslo, Norway
[b] Laboratory of Polymer Chemistry, University of Helsinki, PB 55, FIN-00014 HY, Helsinki, Finland

Received 22 January 2007; received in revised form 28 August 2007; accepted 4 September 2007
Available online 7 September 2007

Abstract

Thermoresponsive associations in aqueous mixtures of the anionic sodium dodecyl sulfate (SDS) surfactant and copolymers of poly(*N*-vinylcaprolactam) and ω-methoxy poly(ethylene oxide) undecyl α-methacrylate (PVCL-g-$C_{11}EO_{42}$) have been characterized using turbidimetry, rheology, and dynamic light scattering (DLS). The cloud point (CP) is shifted toward higher temperature as the percentage of surfactant increases in the PVCL-g-$C_{11}EO_{42}$/SDS mixture, and at low copolymer concentration and high level of SDS addition, the system exhibits a strong polyelectrolyte effect. The polymer concentration dependence of CP in the dilute regime can be described by a power law CP (°C) = $k \times c^{-\nu}$, where the values of k and ν rise with increasing SDS concentration. For semidilute polymer solutions, an abnormal cloud point minimum is observed at a certain polymer–surfactant composition. In the turbidity-temperature curves, a novel anomaly is detected for semidilute polymer solutions at certain levels of surfactant addition. The shear viscosity always exhibits Newtonian behavior even at high polymer concentrations, suggesting that the polymer chains are unentangled and not forming an interconnected network. For semidilute polymer solutions and moderate levels of surfactant addition, the viscosity results indicate a temperature-induced compression of the polymer–surfactant clusters. At a given temperature, high surfactant concentration leads to an expansion of the complexes. DLS results on PVCL-g-$C_{11}EO_{42}$/SDS mixtures at temperatures approaching the CP show the existence of a bimodal relaxation process with a fast mode associated with the diffusion of individual molecules, or small clusters of molecules, and a slow mode portraying interchain aggregation and the formation of aggregates. At temperatures where the systems approach CP, large interchain aggregates are formed. At high SDS concentrations, a temperature increase gives rise to shrinkage of the polymer–surfactant complexes. At this stage, the solvent power is enhanced and together with the repulsive electrostatic interactions the tendency of the system to evolve further interchain associations is suppressed.

Keywords: Thermally responsive graft copolymer; Turbidimetry; Surfactant interactions; Self-assembling; Dynamic light scattering; Rheology

1. Introduction

The self-assembling of thermosensitive amphiphilic copolymers, including block copolymers and graft copolymers, has attracted much interest both for its intrinsic scientific potential and for its technological importance [1–8]. Recently [7], we reported on the structural and dynamical features of aqueous solutions of a neutral thermoresponsive copolymer composed of *N*-vinylcaprolactam and ω-methoxy poly(ethylene oxide) undecyl α-methacrylate (PVCL-g-$C_{11}EO_{42}$). The chemical structure of this polymer is displayed in Fig. 1. This type of thermoresponsive polymer is characterized by a phase separation upon heating, and the system exhibits a lower critical solution temperature (LCST) [9–11]. At low temperature, the solution is homogeneous, but when the temperature exceeds a critical value called the cloud point (CP) of the mixture, a macroscopic phase separation evolves.

The thermosensitive behavior of PVCL-g-$C_{11}EO_{42}$ in aqueous solution depends on the hydrophobic–hydrophilic interplay, which can be readily varied by addition of surfactant molecules,

---

* Corresponding author. Tel.: +47 22855522; fax: +47 22855441.
E-mail address: bo.nystrom@kjemi.uio.no (B. Nyström).

0927-7757/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2007.09.002

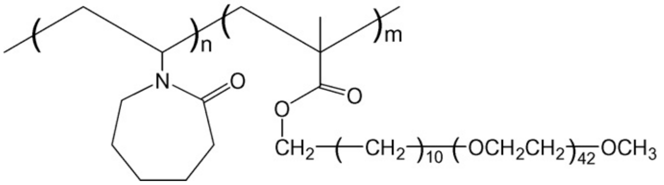

Fig. 1. Illustration of the chemical structure of the grafted PVCL-g-$C_{11}EO_{42}$ copolymer.

such as sodium dodecyl sulfate (SDS). In a recent investigation [8] on this polymer, small angle neutron scattering (SANS) and turbidity measurements revealed that the addition of SDS to aqueous solutions of PVCL-g-$C_{11}EO_{42}$ improved the solvent power through the solubilization of hydrophobic moieties. By changing the temperature and level of surfactant addition, the interplay between intrachain and interchain association can be modulated.

To examine the thermodynamic features and to characterize the dynamics of the association complexes formed in this type of system, we have carried out extensive turbidity, rheological, and dynamic light scattering (DLS) experiments on PVCL-g-$C_{11}EO_{42}$ solutions in the presence of different amounts of SDS and at various temperatures. We report some novel turbidity findings of this system, with an anomalous behavior of the polymer–surfactant mixtures at certain compositions, which has not been reported previously for this type of system. The results from the rheological and DLS measurements show that the competition between intrachain and interchain association of this special thermosensitive copolymer can be tuned by temperature and surfactant concentration. The results provide information about the individual coils and their complexes with ionic surfactants, and temperature-induced association effects. This work reveals that the binding of an ionic surfactant to the polymer gives rise to complex thermodynamics and high levels of SDS addition will reduce the tendency of forming interpolymer complexes. This is an important issue for many practical applications.

2. Experimental

2.1. Materials and solution preparation

The copolymer PVCL-g-$C_{11}EO_{42}$ has been synthesized according to a procedure described previously [7]. The sample has recently been characterized and the weight-average molecular weight determined from light scattering [8] is $M_w = 200{,}000$. The alkyl-poly(ethylene oxide) content has been ascertained by ^1H NMR and is about 15 wt%, i.e., 1.2 mol% [7]. The SDS surfactant was supplied by Fluka Chemie AG, Buchs, Switzerland. It was used without further purification.

Surfactant solutions of different concentrations (millimolal; mm) were prepared by dissolving SDS in double distilled water. Different amounts of polymer were dissolved in these surfactant solutions to obtain the desired polymer concentrations. All samples were prepared by weighing in the components and then stirring the solutions for 1 day at ambient temperature to ensure that the solutions were homogeneous. In the rheology and dynamic light scattering experiments, the samples were allowed to equilibrate for at least 1 h at each measurement temperature before experiments were commenced. The turbidity measurements were carried out at a heating rate of 0.2 °C/min.

2.2. Turbidimetry

The turbidities of the PVCL-g-$C_{11}EO_{42}$/SDS/H_2O solutions were determined with the aid of an NK60-CPA cloud point analyzer from Phase Technology, Richmond, B.C., Canada. The specifications of this instrument and the procedure for the determination of turbidities have been reported elsewhere [8]. The measured signal S from the cloud point analyzer can empirically be related to the turbidity τ, which was determined from measurements of the transmittance on a standard spectrophotometer in a 1 cm cuvette, using the expression $\tau = (-1/L)\ln(I_t/I_0)$, where L is the light path length of the cuvette, I_t is the transmitted light intensity, and I_0 is the incident light intensity. A direct relationship between the calculated turbidity from the spectrophotometer experiments and S from the cloud point analyzer is found [8] to be $\tau = 9.0 \times 10^{-9}\ S^{3.751}$. All data from the cloud point analyzer will be presented in terms of turbidity. The very accurate temperature control of the sample in this instrument and the registration of the diffuse scattered light from the surface of the plate make this a powerful apparatus to monitor turbidity changes in connection with a temperature-induced phase separation. In this study, the heating rate was set to 0.2 °C/min, and no effect of the heating rate on the signal was observed at low heating rates. The cooling (0.2 °C/min) of the samples was also checked, and hysteresis effects were observed for some of the samples. However, due to the vast amount of data this represents, only heating curves are reported in this work.

The turbidity data are analyzed, and cloud points (CP) for the various polymer/SDS compositions are presented. The temperature at which the first deviation of the scattered intensity from the baseline occurred was taken as CP of the considered sample.

2.3. Rheology

Viscosity measurements were performed in a Paar-Physica MCR 300 rheometer using a cone-and-plate geometry, with a cone angle of 1° and a diameter of 75 mm. This rheometer operates effectively with this geometry even on dilute polymer solutions, and the viscosity of water can easily be measured over an extended shear rate domain. The samples were introduced onto the plate, and to prevent evaporation of the solvent, the free surface of the sample was always covered with a thin layer of low viscosity silicone oil (the viscoelastic response of the samples are not observed to be affected by this layer). The measuring unit is equipped with a temperature unit (Peltier plate) that provides a rapid change of the temperature and gives an accurate temperature control (±0.05 °C) over an extended time for all the temperatures considered in this work.

The shear viscosity experiments were conducted over an extended shear rate range, and the results revealed near Newtonian behavior at all polymer concentrations and temperatures.