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Association properties of a high molecular weight poly(propylene oxide-b-ethylene oxide) diblock copolymer in aqueous solution

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Summary

A high molecular weight poly(propylene oxide-b-ethylene oxide) diblock copolymer was prepared via sequential anionic suspension polymerization using a calcium amide-alkoxide initiating system. ^{1}H nuclear magnetic resonance, viscometry and static and dynamic light scattering have been used to characterize the copolymer and to examine its self-assembly in aqueous solution. The copolymer was found to self-associate in a narrow concentration range above a certain critical aggregation concentration. The weight-average molecular weight, the radii of gyration, the second virial coefficients, the diffusion coefficients, and the hydrodynamic radii of the particles in both unimer and aggregate regions were determined. Aggregates of low aggregation number (2-3) were formed. Dynamic light scattering measurements performed in a wide concentration range revealed an enhanced aggregate stability towards dissociation upon dilution.

Introduction

An important class of amphiphilic copolymers which display temperature-induced micellization are the commercially available water-soluble triblock copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO). Considerable interest has been focused on their aqueous solution properties [1-13]. PEO-PPO-PEO and PPO-PEO-PPO (known under trade names Pluronics and Synperonics) are available with molecular weights ranging from 2000 to 20000 g.mol^{-1} and PEO content from 10 to 90 wt. %. Diblock copolymers of PEO and PPO are not readily available; only Booth and co-authors have reported the synthesis and aqueous solution properties of some PEO-PPO diblock copolymers [14,15].

In spite of the fact that the Pluronic copolymers are available in a wide range of molar masses and compositions they cannot satisfy the growing needs for smart polymers suitable for specific applications in technology and medicine. Therefore, more experimental work with other classes of amphiphilic copolymers is required. In the last decade, a large number of high molecular weight (HMW) amphiphilic copolymers have been prepared in our laboratory by means of anionic suspension polymerization using a calcium amide-alkoxide initiating system. The latter has been developed for industrial production of HMW PEO, which is sold by NEOCHIM-Bulgaria under the trade name BADIMOL [16,17]. The materials produced by anionic suspension polymerization using the above initiating system are typically not well defined: they are characterized by a broad molecular weight distribution and composition heterogeneity. These features, together with the ubiquitous clustering in solution, frequently complicate investigations of HMW PEO-based materials and hinder the efforts to fully understand their behavior. Recent results on aqueous solution properties of HMW PEO homopolymers [18] and novel poly(ethylene oxide-b-alkylglycidyl ether) diblock copolymers [19] establish some peculiarities of the behavior of these materials. The results suggest that the coronae of the micelles formed by HMW amphiphiles can be considered as a single separate entity wherein the repulsive forces between the PEO chains and the unimer exchange are greatly diminished [19]. Hence an enhancement of the aggregate stability may be anticipated. Since these amphiphilic block copolymers do not have an analogue as well as for the sake of comparison, in the present work we have directed our attention to the synthesis and investigation of aqueous solution properties of a HMW analogue to the extensively studied Pluronic block copolymers.

Experimental

Materials

Ethylene oxide (Clariant) and calcium (NEOCHIM-Bulgaria) were used as received. Propylene oxide (Aldrich) was distilled over CaH_2. All solvents were purified by standard procedures.

Synthesis and purification of the copolymer

The copolymer was synthesized by sequential ring-opening anionic suspension polymerization of propylene oxide and ethylene oxide in heptane. The preparation of the calcium amide-alkoxide initiating system and the purification of the resulting copolymer have been described elsewhere [16,19].

Solution preparation

Solutions in a wide concentration range were prepared by adding cold ($T < 5$ °C) water provided by purifying unit Milipore Super-Q-System to weighed amounts of the dry bulk copolymer. The samples were kept overnight in a refrigerator at about 3 °C. They were vortexed occasionally and when no macroscopic heterogeneities were visible they were filtered directly into dust-free light scattering cells using 0.2 μm pore-size inorganic filters (Whatman). The light scattering measurements in the low-concentration range were performed at 5 °C immediately after the filtration. For the measurements done at $T > 5$ °C, the solutions were firstly filtered and then heated slowly (~ 5 °C/hour) until the desired temperature was reached.

NMR-spectroscopy

The ^{1}H NMR-spectrum of a ca. 2 wt. % copolymer solution in $CDCl_3$ was recorded on a Bruker WM250 spectrometer operating at 250 MHz. The PPO content of the present copolymer was determined to be 4 wt. %.

Viscometry

The viscosity measurements were carried out with an Ubbelohde type viscometer equipped with a capillary of 0.45 mm diameter and thermostated at 25 °C. The solvent (water) and the solutions were filtered prior to measurements. The constants $K=1.25\times10^{-4}$ dl/g and $\alpha=0.78$ for PEO were used to calculate the viscometric molecular weight [20]. The resulting viscometric molecular weight was 1.46×10^6.

Light Scattering

The weight-average molecular weight (M_w), the z-average radius of gyration (R_g), the second virial coefficient (A_2), the mean diffusion coefficient (D_o), and the hydrodynamic radius (R_h) of the particles were determined by performing simultaneous dynamic (DLS) and static light scattering (SLS) measurements in an experimental setup described earlier [18]. The latter consists of a 488 Ar ion laser and detector optics with an ITT FW 130 photomultiplier and ALV-PM-PD amplifier-discriminator built into a computer. Measurements were made at different angles in the range of 50 – 130° and at different concentrations and temperatures. The refractive index increment (dn/dc) was measured in a differential refractometer with Reyleigh optics. For the present copolymer dn/dc of 0.131 cm^3g^{-1} was obtained.

Results and discussion

Fig. 1 shows the determination of the critical aggregation concentration (cac) of the copolymer at 25 °C using SLS. The excess scattered intensity experiences an abrupt increase with increasing concentration, which suggests the formation of some large structures. A cac of 0.21 g/L was determined, which is at least an order of magnitude lower than the cac of the related Pluronic block copolymers of high PEO content [1,5,9,11-13]. This finding agrees with the trend of a cac decrease with increasing molecular weight at a constant hydrophilic/hydrophobic ratio [21].

The static and dynamic light scattering parameters of the unimers and aggregates were determined in the concentration ranges below and above the cac. In order to avoid the temperature-induced aggregation, the measurements in the unimer region were performed at 5 °C. The relaxation time distributions obtained from DLS are qualitatively similar for both unimers and aggregates: a dominant mode, corresponding to either unimers or aggregates, accompanied by a low-amplitude fast mode (fig. 2). Such distributions are typical for HMW PEO-based materials [18,19]. As concluded earlier [18,19], the fast mode, which is non-diffusive as evidenced by the inset of fig. 2 and considered to derive from internal modes of motion of the copolymer chain, is of marginal interest as far as the determination of the molecular weight is concerned. The dominant modes were found to be diffusive (inset of fig. 2). Following a routine procedure the diffusion coefficients and hydrodynamic radii were determined. The latter for both unimers and aggregates are collected in Table 1.

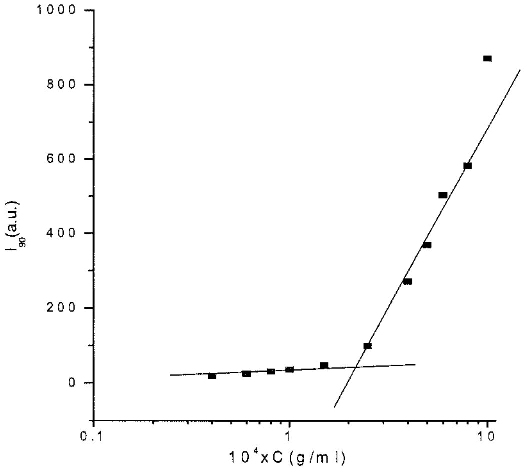

Fig. 1 Variation of the excess scattered light intensity measured at 90°, I_{90}, with the copolymer concentration at 25 °C for the determination of the cac.

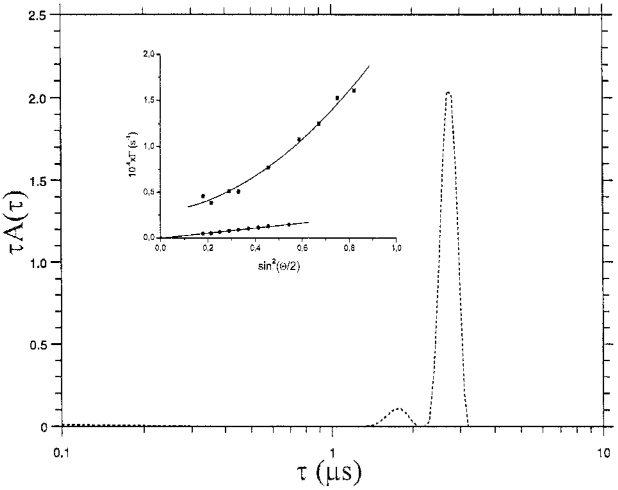

Fig. 2 Relaxation time distribution measured at an angle of 90° and temperature 25 °C of a 0.40 g/L aqueous solution. Inset figure: Relaxation rates, Γ, of the dominant (circles) and fast (squares) modes as a function of $\sin^2(\theta/2)$.

Table 1. Static and dynamic light scattering parameters of unimers and aggregates determined at 5 °C and 25 °C, respectively.

	R_h (nm)	10^4 x A_2 (mol.ml.g^{-2})	R_g (nm)	10^{-6} x M_w (g.mol^{-1})
Unimers	46.7	26.7	39.1	1.40
Aggregates	89.4	-0.55	71.7	3.22

M_w, R_g, and A_2 of the particles in both regions were evaluated using a Zimm plot method. A typical Zimm diagram for the unimer region is presented in fig. 3. The non-linearity in the angular dependence of the reduced scattered light intensity, in particular the slight upward curvature at higher angles for the present system, is usually observed when the product $qR_g < 1$ (here q is the scattering vector) may no longer hold at these angles. The resulting static light scattering parameters are listed in Table 1. It should be noted that the molecular weight of the unimers agrees very well with the viscometric molecular weight. All parameters in Table 1 reflect the aggregation process: A_2 changes from positive to negative, whereas R_h, R_g and M_w are found to increase upon aggregation. However, the size and molecular weight were found to increase roughly by a factor of two in contrast to those of the Pluronic copolymers, which typically rise by one order of magnitude upon the micellization. This feature is attributed to the considerably higher molecular weight of the present copolymer. The aggregation number, N_{agg}, was calculated from the molecular weight data for aggregates and unimers. The resulting value of 2.3 chains per particle is in accordance to the typically low N_{agg} values experimentally found for HMW materials [19,22]. The result is also consistent with the molecular weight dependence of N_{agg} given elsewhere [23]:

$N_{agg} \sim m^{-\upsilon}$

where m is the number of monomer units of the corona-forming block and the negative exponent indicates that N_{agg} decreases with increasing m.

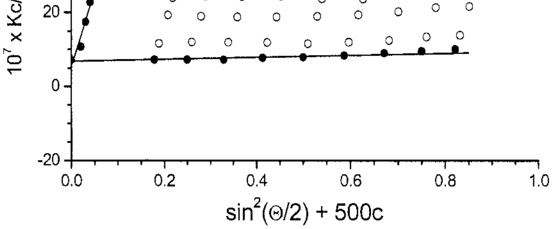

Fig. 3 Zimm plot for the copolymer in the concentration range below the cac and at 5 °C. Experimental points (open symbols), extrapolated points to zero scattering angle and zero concentration (filled symbols).

The kinetic stability of the aggregates is related to the actual rate of their dissociation upon dilution below the cac [21]. In order to test the stability of the aggregates of the present copolymer, a solution with concentration 1.0 g/L, which is above the cac, was diluted to 0.1 g/L (below the cac) and the changes in the relaxation time distribution from DLS were followed with time. No changes in the spectra were detected in the first couples of days and the distributions remained identical to that shown in fig. 2. Approximately a week later a new mode with a relaxation time in good agreement to that of unimers appeared (fig. 4). The results indicate that the dissociation into unimers is a slow process, which probably takes weeks. Importantly, a week after the dilution most of the material is still in the aggregates; using the approach given elsewhere [24,25] the relative weight concentration C_{agg}/C_{uni} was calculated to be about 1.2, which corresponds to 55 % aggregates.

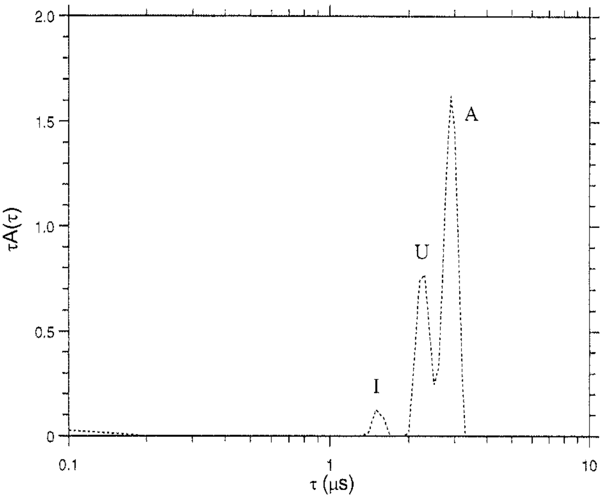

Fig. 4 Relaxation time distribution measured at an angle of 90° and temperature 25 °C of a solution that has been diluted below the cac a week earlier. A, U, and I denote aggregates, unimer, and internal (non-diffusive) peaks, respectively.

Conclusion

The results allow for direct comparison between the properties of the present copolymer and commercially available Pluronic copolymers, in particular these of high PEO content. Similarly to the Pluronic copolymers, the HMW analogue self-associates in a narrow concentration interval. However, the high molecular weight of the present copolymer results in reduction of the cac to the micromolar range. This, in turn, implies that the aggregates exist at very low concentrations. In addition, the aggregates exhibit an enhanced kinetic stability towards dilution below the cac and their disintegration was found to take weeks. In line with the extremely large molecular weight of the copolymer, the aggregates are characterized with low aggregation number in the range 2-3. Upon aggregation the dimensions of the particles were found to increase be a factor of 2.

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