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Study of the temperature-induced aggregation of polyoxometalate-poly(*N,N*-diethylacrylamide) hybrids in water

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ABSTRACT

In this article, we study the temperature-induced phase transition of aqueous solutions of tailor-made Dawson polyoxometalate-poly(*N,N*-diethylacrylamide) hybrids (POM-PDEAAm) by means of differential scanning calorimetry, dynamic light scattering and cryo-TEM microscopy. Generally, the typical thermoresponsive aggregation of the PDEAAm in water was transferred to the hybrids. The organization of the compounds in solution below and above the transition temperature was studied, and precious insights in the aggregation mechanisms were obtained. The impact of the polymer chain-ends, the nature of the counterions of the negatively charged POM subunits and the weight fraction of the POM was elucidated, revealing a strong influence of the POM's counter-ions. Temperature and nature of the cations are thus two external factors that can be used to control the properties of the conjugates.

1. Introduction

Polyoxometalates (POMs) are negatively charged metal-oxygen clusters of early transition metals in high oxidation states (most commonly V^{V}, Mo^{VI} and W^{VI}) which have important electronic and chemical properties making them suited for applications in catalysis and materials science [1–4]. Synthetic methods have been devised to obtain organo-POMs [5–7]. A particular case constitutes polymer-POM hybrids that combine the characteristics of polymers with that of their inorganic counterparts [8]. However, only a limited number of examples of covalently linked POM-polymer conjugates have been reported in the literature [9–11], and even less studies have been dedicated to their physicochemical characterization. Depending on the method used, POM units can be randomly distributed along the polymer backbones or be localized at their chain end. In the latter case, the inorganic and organic subunits are well-separated, making them especially appealing for self-assembly into nanostructured materials [11c]. In view of their potential applications, hybrids systems of which the assembly might be externally tuned seem particularly appealing. [11c,12].

As an example, Wang's group synthesized a POM-polystyrene hybrid composed of a $\{(Bu_4N)_5[H_4P_2W_{15}V_3O_{62}]\}$ Dawson vanadotungstate head and a polystyrene (PS) tail *via* ATRP (atom transfer radical polymerization) [13]. The proton salts of the obtained POM-PS composite formed aggregates in DMF, which showed a transition from vesicles to tubular structures upon thermal annealing, these latter being thermodynamically more stable [14]. Hitherto very few stimuli-responsive covalent POM-polymer hybrids have been studied [12,15].

We had reported previously [11e] the synthesis of an α_2-substitued Dawson phosphotungstate grafted by a poly(*N,N*-diethylacrylamide) (PDEAAm) oligomer $[\alpha_2\text{-}P_2W_{17}O_{61}SnCH_2CH_2C(=O)NHCH_2\text{-poly}(N,N\text{-diethylacrylamide})]^{7-}$, where the molar mass of the short polymer chain was in the same range as that of the inorganic cluster (about 5 kg mol^{-1}). Subsequently we reported the preparation of a series of water-soluble POM-PDEAAm hybrids *via* RAFT polymerization and demonstrated their catalytic activity imparted by the α_1-substituted Dawson phosphotungstate $[\alpha_1\text{-}P_2W_{17}O_{61}\{Sn(CH_2)_2C(O)NH(CH_2)_3R\}]$ [16]. In both cases, poly(*N,N*-

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diethylacrylamide) (PDEAAm) had been selected as the polymer component for its temperature-dependent solubility in water [17,18], a feature that characterizes it as smart material. Upon heating PDEAAm solutions above its transition temperature (TT), phase separation occurs and the polymer chains may form colloidally stable aggregates, called mesoglobules [18]. This feature results from the temperature dependency of hydrogen bonds and hydrophobic interactions, and viscoelastic effects.

We study herein in detail this thermally-induced phase transition of our α_1-substituted Dawson phosphotungstate-PDEAAm hybrids by means of differential scanning calorimetry (DSC), dynamic light scattering (DLS) and cryo-TEM (Scheme 1), and discuss the impact of polymer molar mass, solution concentration and counterions associated to the POM on the transition.

2. Experimental section

2.1. Materials

PDEAAm (PX) and POM-PDEAAm hybrid, tetrabutylammonium (TBA) salts, (PPX-T) samples were synthesized as reported before [16]. Their characteristics are reported in Tables 1 and 2. The molar mass of the hydrophobic POM-TBA salt is $MW_{\text{POM-TTC–T, TBA}} = 6537\ \text{g mol}^{-1}$ and that of the hydrophilic NH_4^+ one is $MW_{\text{POM-TTC-N, NH4}} = 4966\ \text{g mol}^{-1}$.

2.2. Ion exchange: synthesis of $(NH_4)_7[\alpha_1\text{-POM}]$-PDEAAm

In a typical example, a solution of NH_4PF_6 (3.57×10^{-5} mol, 20 equiv, 6 mg) in acetonitrile (1 mL), which had been filtered on cotton before use, was added to a solution of hybrid PP55-T (1.78×10^{-6} mol, 1 equiv, 100 mg) in acetonitrile (3 mL) under nitrogen atmosphere. The solution was concentrated *in vacuo* and redissolved in a minimum of acetonitrile. It was then precipitated upon addition of Et_2O, and the solid was isolated by centrifugation. This process was repeated three times. The solid was washed with pure Et_2O and dried *in vacuo* to obtain a white solid (91.8 mg, 95% yield). It should be noted, that the final product contained still important amounts of NH_4PF_6. Its quantity was estimated by ^{31}P NMR to 44 equivalents relative to the POM unit. ^{31}P NMR (121.5 MHz, CD_3CN): δ −143.2 (sept, PF_6^-), δ −11.9 (s, 1 P, PW_9), −6.5 (s + d, 1 P, $J_{SnP} = 41.5$ Hz, PW_8Sn).

2.3. Removal of the thiocarbonylthio end group from PDEAAm-C_{12}: synthesis of P55-H according to reference [11e]

150.0 mg of PDEAAm-C_{12} ($M_n = 47.3\ \text{kg mol}^{-1}$, $M_w/M_n = 1.18$, 0.003 mmol, 1.0 eq.) were dissolved in 1 mL propan-2-ol and heated under reflux to 80 °C. A solution of lauroyl peroxide (1.6 mg, 0.004 mmol, 1.3 eq.) in propan-2-ol (0.4 mL) and toluene (0.1 mL) was added in seven portions every 3 h under a nitrogen atmosphere. The reaction mixture was then precipitated in cold pentane (88.6 mg, 59%, $M_{n,LS}$ (SEC) = 47.7 kg mol^{-1}, M_w/M_n (PMMA) = 1.18).

2.4. Instrumentation

2.4.1. Differential scanning nanoCalorimetry (nanoDSC)

Calorimetric measurements were done with an N-DSC III instrument from Calorimetry Sciences Corporation at a scan rate of 0.5 °C min^{-1}. The system consists of two capillary cells, respectively reference and sample, of 0.3 mL under pressure 5×10^5 Pa. Samples of a concentration of 5 mg mL^{-1} were prepared and stirred during one day before analysis. All samples were degassed under reduced pressure before injection and were not capped. They were equilibrated for 10 min before each heating and cooling run, going from 5 °C to 85 °C. First, a baseline scan (water in both the reference and the sample cells) was recorded in identical conditions and subtracted from the sample scan. The transition temperature was determined at the onset of the transition, T_{onset}, *i.e.* the intersection of the baseline and the leading edge of the endotherm, and the transition enthalpy (ΔH) of the polymers was calculated by integrating endotherms at the second heating run (see Figure SI-1) [19]. The error on the enthalpy of the endotherms was estimated to be in the range of 5%.

2.4.2. Dynamic light scattering

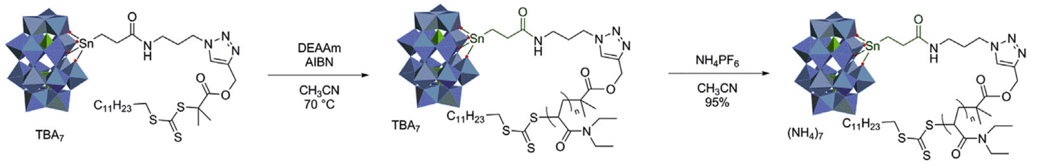
Dynamic light scattering (DLS) measurements were carried out using a Zetasizer Nano S90 from Malvern using a 5 mW He–Ne laser at 633 nm at 20 °C and 70 °C. The samples' concentration was generally 5 mg mL^{-1}, *i.e.* the same used for the determination of calorimetric measurements with nanoDSC. To investigate the influence of the concentration, some samples were studied at different concentrations: at 1 mg mL^{-1}, 5 mg mL^{-1} and 10 mg mL^{-1}. The solutions were dissolved and stirred during one day before analysis. Results were obtained in duplicate.

2.4.3. Cryo-TEM

Cryo-Transmission Electron Microscopy (cryo-TEM) was used to determine the shape and size of the POM-polymer hybrids. Two types of cryo-TEM analyses were performed: To analyze solutions below the transition temperature (TT) of PDEAAm, 4 µL of an aqueous solution of POM-polymer (5 mg mL^{-1}) was deposited at room temperature on a quantifoil grid and rapidly frozen in liquid ethane. In the second case, the aqueous POM-polymer solution was heated until it became turbid, rapidly deposited on a quantifoil grid and then rapidly frozen in liquid ethane. The grids were transferred and observed at −180 °C on a JEOL JEM-2100 LaB6 microscope operating at 200 kV under low-dose conditions (less than 10 electrons Å^{-2} s^{-1}) at a nominal magnification of 20 000 and 40 000. Images were recorded on a 2k by 2k pixels CCD camera (Gatan Ultrascan 1000).

2.4.4. Size exclusion chromatography (SEC)

Size exclusion chromatography measurements were performed with a Viscotek Tetra Detector Array (TDA) including a differential refractive index detector (RI), a right (90°) and a low (7°) angle light scattering (LS) detector (RALS/LALS), a four-capillary differential viscometer, and a diode array UV detector. DMF (+LiBr, 1 g L^{-1}) was used as the mobile phase at a flow rate of 0.8 mL min^{-1} and toluene



Scheme 1. Synthesis pathway towards POM-PDEAAm hybrids [16].