



Fluorinated oligo(ethylene glycol) methacrylate-based copolymers: Tuning of self assembly properties and relationship with rheological behavior



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ABSTRACT

A series of thermo-responsive oligo(ethylene glycol) methacrylate (OEGMA, $M_n = 300$ g/mol)-pentafluorostyrene (PFS) copolymers was prepared, and the effect of composition on polymer conformation changes and size of the self-assembled particles in solution was studied. Furthermore, the relationship between self-aggregation mechanistic steps in water and rheological properties is reported. Water-soluble OEGMA-PFS copolymers were synthesized at different molar ratios *via* free radical polymerization, and their phase transition behavior was investigated in detail by dynamic light scattering (DLS), ¹H NMR, simultaneous rheometry-FTIR spectroscopy, and transmission electronic microscopy (TEM). All copolymers exhibited sharp and reversible LCST in water. LCST and particle size of the self-assembling copolymers can be precisely tuned by varying monomer molar ratio. Simultaneous rheometry-FTIR spectroscopy showed that above the LCST, copolymers with higher OEGMA content form micron-sized and hydrated particles, resulting in a pseudo-hydrogel structure. When the hydrophobic character increases, a more significant dehydration of OEGMA side chains leads to a strengthening of polymer chain interactions, resulting in the formation of nanosized and phase-segregated particles. These results are also relevant with a view of using these structures as a template for the preparation of chemically or physically stabilized nanoparticles to be employed for a variety of applications, such as immobilization, controlled release and flocculation in water treatment.

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1. Introduction

Polymeric micro- and nano-particles play a pivotal role in a wide spectrum of application fields ranging from electronics to sensors, medicine, biotechnology, and environmental technology [1,2]. Properties of polymer particles, such as morphology, size, and shape, strictly depend on the preparation method, and are crucial in view of specific applications. Therefore, reliable synthesis of particles with tuneable properties is of great importance.

Thermo-responsive polymers are widely employed for the preparation of micro- and nano-sized particles [3–5]. The majority

of thermo-responsive polymers displays a lower critical solution temperature (LCST) in aqueous solution. Below the LCST, polymer chains are soluble in water and exist in a random coil conformation due to hydrogen-bonding interactions between polymer and surrounding water molecules. When temperature exceeds the LCST, these interactions are disrupted, and attractive forces between hydrophobic segments become dominant. This causes polymer chains to collapse and form nanoaggregates, resulting in a macroscopic clouding of the solution [6]. The LCST value is determined by a balance between attractive segment-water and segment-segment interactions. In general, structural factors that increase segment-segment interactions decrease LCST; those increasing segment-water interactions increase LCST [7]. In this frame, the temperature is used as a simple external trigger for controlling hydrophilicity, and therefore the structural shape of these macromolecules. The capability to self-assemble in water, thus generating nanoscale

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micellar structures in dilute solutions, may be particularly interesting for several applications such as nanoreactors or nanovehicles in biology related fields [8,9]. On the other hand, self-assembled micrometer-sized aggregates have demonstrated potential applications including actuators, bioseparation, enzyme immobilization, and catalysis [10,11].

Recently, many researchers have focused their attention on thermo-responsive properties of polymers based on oligo(ethylene glycol) methacrylate (OEGMA), which have methacrylate backbone and poly(ethylene glycol) branches. These copolymers can show tunable LCST values, in the range of 30–90 °C, a reversible phase transition and bioinert properties [12]. The balance between hydrophilic and hydrophobic moieties in such polymer structure has a strong effect on the LCST. In general, incorporation of hydrophobic comonomers leads to lower LCST, while hydrophilic comonomers increase the LCST. Therefore, the possibility of controlling the LCST by varying monomer composition represents an important and useful feature of OEGMA-based copolymers. Many studies on the synthesis and self-assembly of amphiphilic brush-like copolymers of OEGMA have been reported [13–22].

Among non-polar monomers, fluorinated units are the most hydrophobic, and their tendency to separate from water or hydrophilic groups is the strongest [23]. The synthesis of fluorinated thermo-responsive copolymers allows to fine tune LCST and self-assembly properties. Several fluorinated OEGMA-based copolymers have been previously synthesized by controlled radical polymerization (CRP) methods. Zhang et al. [7] prepared thermo-responsive copolymers based on OEGMA and 2,2,2-trifluoroethyl acrylate (TFEA) *via* reversible addition-fragmentation chain transfer polymerization (RAFT). LCST values between 73 and 45 °C were found, depending on the weight fraction of hydrophobic monomer. Partially-fluorinated copolymers of OEGMA and perfluorooctyl methacrylate (OEGMA-*co*-FOMA) have been also described, and the dependence of the phase transition temperature on fluorine content in liquid CO₂ has been examined [24]. Among fluorinated monomers, pentafluorostyrene (PFS) has been employed to develop brush-type amphiphilic diblock copolymers with OEGMA (P(OEGMA-*b*-PPFS)) *via* atomic transfer radical polymerization (ATRP) to be applied as antibiofouling coatings [25,26]. However, the possibility of a facile nucleophilic substitution of the para-fluorine makes PFS a versatile building block to provide further functionalities to the resulting polymer. In this regard, PFS homopolymers and random copolymers with OEGMA ($M_n = 475$ g/mol) have been reported, in which the PFS moieties were further reacted with thiophenol to increase copolymer hydrophobicity. This allowed to decrease the cloud point from 55 to 33 °C [27]. Along the same lines, glycopolymers of styrene (St) and PFS have been synthesized by a combination of nitroxide-mediated polymerization and “click” chemistry involving para-fluorine substitution [28].

In spite of the considerable attention paid to thermo-responsive fluorinated copolymers, their self-assembly properties have not been studied in detail, as concerns the relation between copolymer composition and size of the resulting aggregates [29]. Controlling particle size is of prime importance with a view of using the self-assembled aggregates as a template for the preparation of stabilized nanoparticles [30]. In the case of PFS-based copolymers, this goal can be achieved taking advantage of the demonstrated para-fluorine reactivity. Therefore, in the present work self-assembling copolymers of OEGMA ($M_n = 300$ g/mol) and PFS (P(OEGMA-*co*-PFS)) at different compositions were synthesized *via* free radical polymerization (FRP). FRP was chosen as it allows achieving higher molecular weights compared to living polymerization methods, then potentially resulting in a decrease of LCST. Moreover, FRP is easier to scale up and more cost effective with respect to living

polymerization, not requiring transition metal catalysts or bimolecular exchange with sulfur-based compounds. Size and morphology of nanoparticles resulting from copolymer self-assembly were investigated by dynamic light scattering (DLS) and transmission electron microscopy (TEM). The mechanism of thermally-induced aggregation in water was thoroughly studied by nuclear magnetic resonance (¹H NMR) and simultaneous rheometry-infrared spectroscopy (Rheo-FTIR), to get insight on the effect of composition on the thermally-driven conformational and rheological changes of polymers in solution.

In this regard, rheometry has been used to elucidate the sol–gel transition and gel characteristics of aqueous solutions of thermo-sensitive (ethyleneglycol) acrylate and OEGMA-based copolymers [31–33]. However, to our knowledge the relation between self-aggregation mechanistic steps of thermo-responsive polymers and evolution of their rheological properties is reported here for the first time.

2. Experimental

2.1. Materials

Pentafluorostyrene (PFS, 99%, Sigma-Aldrich) and oligo(ethylene glycol)methyl ether methacrylate (OEGMA, $M_n \sim 300$ g/mol, Sigma-Aldrich) were purified by passing over a neutral aluminum oxide column. Trioxane (99%), benzoyl peroxide (BPO, 98%), dimethylformamide (DMF, 99.8%), petroleum ether (ACS reagent), and tetrahydrofuran (THF, 99.9%) were from Sigma-Aldrich and used as received.

2.2. Polymerization of OEGMA and PFS

The synthesis of PFS and OEGMA homopolymers (PPFS and POEGMA, respectively) and copolymers P(OEGMA-*co*-PFS), herein referred to as PFG, was performed *via* radical polymerization under nitrogen in DMF (in the case of PFS homopolymerization, a mixture of DMF and toluene (7:3 v/v) was used as solvent to inhibit precipitation of the growing polymer). Feeding molar ratios used and codes of the copolymers obtained are reported in Table 1.

In a typical copolymerization reaction (referred to the PFG25 copolymer), 4.32 g (14.4 mmol) of OEGMA, 0.933 g (4.8 mmol) of PFS, 0.288 g (3.2 mmol) of trioxane, 0.0093 g (0.4 mmol) of BPO and 40 mL of DMF were introduced in a Schlenk tube under nitrogen and stirred for 15 min. The mixture was divided into several tubes and bubbled with nitrogen for 5 min. The flasks were then stoppered and placed in a preheated oil bath at 100 °C. To evaluate monomer conversion during reaction, the tubes were taken at fixed times over the course of polymerization, and placed into ice to quench the reaction. At the end of the reaction, the reaction mixture was dried and dissolved in THF, then precipitated and washed with petroleum ether. Copolymers were dried under vacuum at room temperature until constant weight.

2.3. Polymer characterization

¹H NMR spectra were recorded in CDCl₃ or D₂O on a Bruker Avance III 400 MHz spectrometer. Solution spectra were measured under the following measurements conditions: 90° pulse width 7.5 μs, relaxation delay 1 s, acquisition time 1.4 s, and 16 scans. Purified copolymers were analyzed by ¹H NMR in both CDCl₃ and D₂O in order to study the molecular arrangement of polymer chains in the two solvents.

Gel Permeation Chromatography (GPC) was performed to determine molecular weight distributions, using a GPC Max Vis-cotek system equipped with a TDA 305 triple detector, and

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