



## New fluorinated hybrid organic/inorganic water soluble polymeric network



Arnaud Zenerino<sup>a</sup>, Sonia Amigoni<sup>a</sup>, Elisabeth Taffin de Givenchy<sup>a</sup>, Denis Josse<sup>b</sup>,  
Frédéric Guittard<sup>a,\*</sup>

<sup>a</sup> Univ. Nice Sophia Antipolis, CNRS, LPMC UMR 7336, Surface & Interface Group, Parc Valrose, 06100 Nice, France

<sup>b</sup> Institut de recherche biomédicale des armées, département de toxicologie, unité protection-décontamination, 24 avenue des maquis du grésivaudan, 38700 La Tronche et Service Départemental d'Incendie et de Secours des Alpes-Maritimes, 140, Avenue de Lattre de Tassigny BP99, 06271 Villeneuve Loubet Cedex, France

### ARTICLE INFO

#### Article history:

Received 19 April 2013

Received in revised form

27 August 2013

Accepted 28 August 2013

Available online 7 September 2013

#### Keywords:

HASE

Nanoparticles

Dispersion

### ABSTRACT

This work presents the elaboration of nanoparticle networks from HASE (hydrophobically alkali-soluble emulsion) thickeners grafted with silica nanoparticles. Three HASE were realized by copolymerization in emulsion of methacrylic acid and ethyl acrylate or trifluoroethyl methacrylate and a hydrocarbon or fluorocarbon macromonomer. The macromonomer contains a hydrophobic pendant group separated from the backbone by a polyethylene glycol spacer chain. The free acid functions of the copolymer were coupled with amine functionalized silica nanoparticles. In basic aqueous solutions, the suspensions containing 1 wt.% of this polymer/SiO<sub>2</sub> nanocomposite characterized by DLS (size analysis) and Cryo-SEM are stable, translucent, and gel-like at pH = 7.5. Rheological measurements demonstrated that the grafting of silica nanoparticles did not affect the thickening effect of precursor co-polymers. Coating of glass plates was realized with these hybrid networks and characterized by AFM, indicating that the silica nanoparticles were more homogeneously dispersed when a fluorocarbon co-polymer was used.

© 2013 Elsevier Ltd. All rights reserved.

### 1. Introduction

Grafting of inorganic nanoparticles to polymer has been extensively used to improve the spatial distribution of nanoparticles in nanocomposites. This allowed to increase the stability and dispersibility of nanoparticles in various solvents and polymer matrices for numerous applications [1–11] and to get new functional materials with enhanced thermal and mechanical properties. In a fabrication process, the control of nanoparticles dispersion into a polymer matrix is an important point to limit the nanoparticles aggregation and preserve the final material properties. Efficient dispersion could be obtained with chemical or physical modification of nanoparticle surfaces [11–16]. Typically, the combination of inorganic compounds to organic hydrophobic compounds, such as fluorinated polymers, remains a challenge in surface coatings in order to obtain low surface tension materials able to repel liquids such as water and oil [2,6,17–19].

Associative polymers, such as hydrophobically modified alkali-soluble emulsion (HASE) have the ability to form three-

dimensional network gels. The backbone of these copolymers is constituted of methacrylic acid (MA), ethyl acrylate (EA) and a small amount of associative macromonomer (M). The macromonomer contains a hydrophobic pendant group separated from the backbone by a polyethylene glycol (PEG) spacer chain. In basic aqueous solution, the co-polymers thicken and their hydrodynamic volume increases [20]. At pH above 7, the polymer becomes soluble in water and expands due to repulsions of the carboxylate anions from MA monomers. Moreover the hydrophobic groups associate to form a gel-like network that enhances the solution viscosity at low shear rates [21,22]. The substitution of hydrocarbon moieties into fluorinated ones in the co-polymer leads to very low surface tension copolymers, and often improves the dispersibility of nanoparticles in water [20,21,23–26]. Our recent works demonstrated that the total replacement of ethyl groups in an HASE skeleton by trifluoroethyl groups led to solutions with a thickening effect equivalent to the reference hydrocarbon HASE [27].

In this work, our goal was to graft silica nanoparticles onto an associative thickening polymer HASE in order to get homogeneously dispersed silica nanoparticles suspension in water. According to our results, the covalent linkage of nanoparticles is also interesting to decrease their environmental toxicity [28].

\* Corresponding author. Tel.: +33 0492076159; fax: +33 0492076156.  
E-mail address: [guittard@unice.fr](mailto:guittard@unice.fr) (F. Guittard).

In order to evaluate the impact of fluorocarbon chains on the dispersion of the grafted nanoparticles in aqueous medium, we described first the synthesis of a new HASE co-polymer containing hydrocarbon or fluorocarbon macromonomer and trifluoroethyl acrylate or EA.

Silica nanoparticles functionalized with amine groups were covalently attached to the carboxylic functions of the co-polymer with a coupling agent in water (Fig. 1). The carboxylic functions of the co-polymer brought by the MA were the grafting sites of the nanoparticles and were also responsible for the swelling of the thickening agent. As a consequence the dispersibility of nanoparticles in water could depend on the balance between the level of grafting and the number of free  $-\text{COOH}$  functions in the co-polymer. The suspension in water of our new hybrid organic/inorganic materials was characterized by using Dynamic Light Scattering (DLS) and Cryo-Scanning Electron Microscopy (Cryo-SEM).

## 2. Experimental section

**Synthesis.** Undecanoic acid (98%, Aldrich), 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptafluoroundecanoic acid,  $N,N'$ -dicyclohexylcarbodiimide (DCC, >99%, Fluka), (polyethyleneglycol)monomethacrylate (PEGMM, average  $M_n$  500, Aldrich), dichloromethane anhydrous (>99.8%, Sigma–Aldrich), methacrylic acid (MA, 99%, Aldrich), ethyl acrylate (EA, 99%, Aldrich), trifluoroethyl methacrylate (TFEM, Arkema), sodium dodecyl sulphate (SDS, >99%, Sigma–Aldrich), potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ , >99%, Sigma–Aldrich), acetone (>99.5%, Sigma–Aldrich), silica fumed of 14 nm diameter (Sigma–Aldrich), (3-aminopropyl)triethoxysilane (99%, Aldrich),  $N$ -(3-dimethylaminopropyl)- $N'$ -ethylcarbodiimide hydrochloride (EDC, Sigma–Aldrich),  $N$ -hydroxysuccinimide (NHS, 98%, Aldrich), toluene (anhydrous, 99.8%, Sigma–Aldrich), tetrahydrofuran (THF, >99.9%, Sigma–Aldrich) and dimethyl sulfoxide- $d_6$  (99.9 atom % D,

Aldrich) were used as received. Deionized water was used for all emulsion polymerizations and grafting reactions.

**Instrumentation.** IR spectra were carried out with a Perkin Elmer (United States of America) Spectrum 100 FT-IR spectrometer by potassium bromide pellet method. NMR spectra were measured on a Bruker W-200 MHz. The glass temperatures and melting points were determined with Jade DSC from Perkin Elmer calibrated with indium and zinc. Samples were heated from  $-40$  to  $300$  °C with a rate flow of  $10$  °C/min. The number-average molar masses ( $M_n$ ), the weight-average molar masses ( $M_w$ ) and the molar mass distributions (polydispersity index:  $\text{PDI} = M_w/M_n$ ) were determined by size exclusion chromatography (SEC) equipped with  $2 \times [\text{PLGelMixed-C } 300 \times 7.5 \text{ mm} - 5 \mu\text{l}] + \text{pre-column PL Gel } 5 \mu\text{m}$  and calibrated with polystyrene compounds. THF was used as the eluent at a flow rate of  $1$  mL/min at  $25$  °C. Approximately  $5$  mg of the polymer was weighed into a glass vial, to which  $1$  mL of THF was added. SEC profiles are provided in [Supplementary data](#) showing a broad monomodal distribution for HASE-F copolymer. Transmission Electronic Microscopy image was realized with a  $120$  kV JEOL JEM-1400 (Japan). Cryo-Scanning Electron Microscopy (Cryo-SEM) images were realized with a JEOL 6700F microscope (Japan). One drop of the sample was rapidly frozen in nitrogen slush at  $-220$  °C and transferred under vacuum in the cryofracture apparatus (Alto 2500 GATAN, UK) chamber where it was fractured at  $-100$  °C and maintained at this temperature during  $7$  min for sublimation. It was then metallized with AuPd and introduced into the microscope chamber where it was maintained at  $-100$  °C during the observation. The rheological measurements were carried out with a Physica MCR 51 rheometer (from Anton Paar, Austria) with a cone-and-plate measuring system having a diameter of  $49.953$  mm and a cone angle of  $1^\circ$ . Experiments were performed at  $20$  °C and samples were analysed in solution of  $1$  wt.% at  $\text{pH} = 8$ . Strain measurements were performed at a frequency of  $1$  Hz in the strain region varying

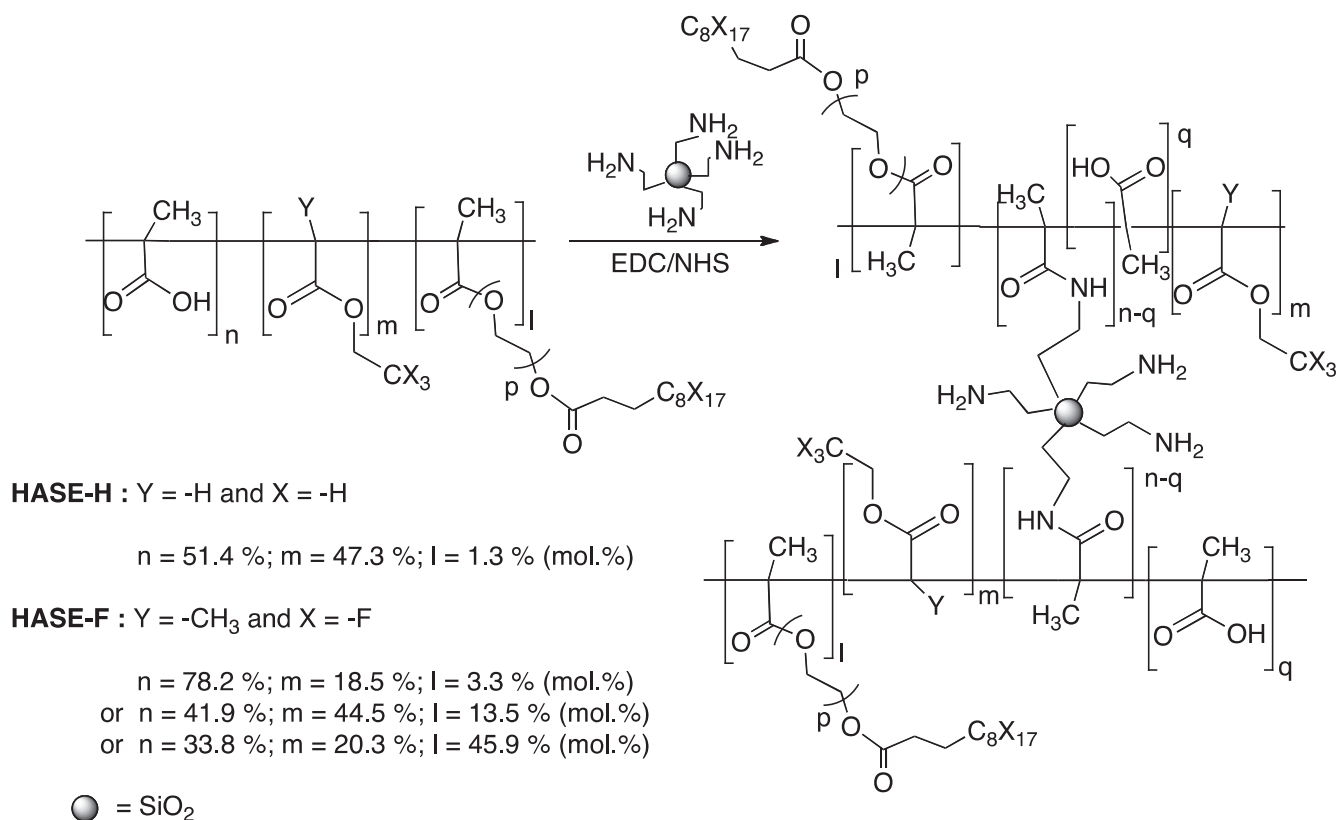


Fig. 1. Synthesis of the organic/inorganic polymeric network.

Download English Version:

<https://daneshyari.com/en/article/5181553>

Download Persian Version:

<https://daneshyari.com/article/5181553>

[Daneshyari.com](https://daneshyari.com)