ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Journal of Colloid and Interface Science 306 (2007) 398–404

Journal of
Colloid and
Interface Science

www.elsevier.com/locate/jcis

Controlled synthesis and association behavior of graft Pluronic in aqueous solutions

Y. Zhang, Y.M. Lam [*]

School of Material Science and Engineering, Nanyang Technological University, Nanyang Drive, 639798 Singapore

Received 19 June 2006; accepted 27 October 2006

Abstract

Poly(vinyl pyrrolidone) (PVP) was grafted onto Pluronic F127 (PEO–PPO–PEO) to produce novel amphiphilic PVP–g–F127 graft copolymers. A controlled synthesis method was used to graft PVP onto different parts of F127. Two types of graft polymers were obtained: one has PVP grafted onto the PEO part of F127 and the other has PVP grafted onto the PPO part of F127. The association behavior of the two modified polymers was examined using differential scanning calorimetry, surface tension measurements, and dynamic light scattering.

Keywords: Pluronic; Graft copolymer; Poly(vinyl pyrrolidone); ^{1}H NMR; Surface tension (ST); Dynamic light scattering (DLS)

1. Introduction

Poly(ethylene oxide)–b–poly(propylene oxide)–b–poly(ethylene oxide) triblock copolymers are of commercial importance and also excite academic interest on account of their association properties in aqueous solution. Pluronic or Poloxamer (BASF) and Synperonic (ICI) polyols are the commercial names that find widespread industrial applications as emulsifying, wetting, thickening, coating, solubilizing, stabilizing, dispersing, lubricating, and foaming agents [1–5]. The association characteristics of Pluronic, such as critical micellization concentration, critical micellization temperature, association number, micelle size, and thermodynamic properties [6–10], in the dilute regime have been widely and deeply investigated by many researchers.

In recent studies, researchers have paid more attention to the modification of Pluronic to improve its properties and obtain broader applications. One of the reasons that chemical modifications of Pluronic block copolymers are carried out is its critical micelle concentration. A good example is F127, which has a relatively high CMC due to the low hydrophobicity of PPO blocks. The Pluronic copolymers have been hydrophobically modified with polycaprolactone (PCL) [11,12]. The copolymers PCL–Pluronic–PCL are synthesized by the ring-opening polymerization of the monomer ε-caprolactone using the Pluronic copolymers as the initiator and stannous octoate ($Sn(Oct)_2$) as the catalyst. The PCL–Pluronic–PCL copolymers can self-assemble into micelles in water at lower CMC than Pluronic copolymer. The size of micelles decreases with increasing temperature. This may be attributed to the hydrophobicity of the PPO block, which increases with increasing temperature. Hence, the interaction between the PCL block in the core and the PPO block in the shell is strengthened. Bromberg [13,14] has synthesized PEO–PPO–PEO block copolymers with poly(acrylic acid) (PAA), thereby imparting a dual responsive property (i.e., pH and temperature) to the polymer by dispersion/emulsion polymerization. The PEO–PPO–PEO–g–PAA graft polymer has a high molecular weight and extreme temperature sensitivity. Compared with Pluronic copolymers, the graft copolymers can form reversible gels with significant elastic moduli in water at lower concentration above a certain temperature. Apart from these few studies, little research has been conducted on the chemical modification of Pluronic block copolymer.

PVP is a well-known water-soluble, biocompatible, and relatively amphiphilic polymer. The highly polar amide confers hydrophilic and polar attracting properties on the polymer, while the apolar methylene group in the backbone and the methine

---

[*] Corresponding author. Fax: +65 67909081.
E-mail address: ymlam@ntu.edu.sg (Y.M. Lam).

0021-9797/\$ – see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2006.10.073

group in the ring contribute to its hydrophobic properties [15]. Since PVP was discovered, the applications of PVP have increased tremendously. Murnper and Alain [16] reported the use of PVP as a protective agent during plasmid delivery to muscle. Ziebell et al. [17] studied the extent of the binding affinity of PVP toward small molecules in aqueous solution. Other applications [18] took advantage of certain PVP properties, such as water solubility and formation of complexes with anion and neutral organic molecules.

Pluronic micelles, which are used to solubilize low-molecular-mass drugs, such as polypeptides, are being actively investigated as a potential drug delivery system [19–23]. Since PVP is itself a lyoprotectant, it should self-assemble in micelles, with excellent storage properties, and should be able to incorporate a variety of drugs into the inner core and the outer shell, with a high loading capacity.

The objective of the present study was to synthesize such novel graft copolymers and compare the solution behavior of the novel graft copolymers to that of the ungrafted polymers. The novel graft copolymer, F127–g–PVP, is designed to integrate the benign nature of the two polymers. It will have excellent properties when interacting with various additives.

2. Experimental

2.1. Materials

Pluronic F127 was purchased from Fluka and used without further purification. It has the formula $EO_{100}PO_{65}EO_{100}$ and a nominal molecular weight of 12,600. The molecular weight of the PPO segment is 3780 and 70 wt% of the chain is made up of PEO. *N*-vinyl pyrrolidone (VP) obtained from Fluka was distilled at 100 °C before use.

Lauroyl peroxide (LP) (97%, redox initiator) and ammonium persulfate (98%) were obtained from Lancaster. Heptane and cyclohexane (HPLC grade) were purchased from Fisher company and used without further purification. Acetone (HPLC grade) and THF (HPLC grade) were obtained from Baker and were used as received. Poly(vinylpyrrolidone–co-1-hexadecene) (GanexV216) (dispersion stabilizer) was supplied courtesy of International Specialty Products (Wayne, NJ) and used as received.

2.2. Synthesis of F127–g–PVP graft copolymers

Vinyl pyrrolidone and dodecane were first distilled at 100 °C and then kept in sealed bottles. The rest of the chemicals were used as received unless specified. Dodecane was distilled to eliminate impurities that may have negative effects on polymerization.

Two methods of graft polymerization were used.

Method 1. F127(PPO)–g–PVP was first synthesized by dispersion polymerization. Synthesis was carried out on a laboratory scale. Pluronic (6 g) was dissolved in vinyl pyrrolidone (13 ml) under constant nitrogen purging. Lauroyl peroxide (25 mg) and 4,4′-azobis(cyanovaleric acid) (25 mg) were dissolved in 2 ml of vinyl pyrrolidone and added to the resulting solution. The resulting solution was deaerated by nitrogen bubbling for 0.5 h and added to a 250-ml three-necked flask containing 60 ml of 1 wt% solution of Ganex V-216 in dodecane. The flask was vigorously stirred by a magnetic stirrer and deaerated by constant nitrogen purging from the bottom. Then the flask was heated to 70 °C using an oil bath and kept at that temperature under constant stirring and nitrogen purging. The reaction was continued for 6 h. Then the reaction was stopped, and the contents of the reactor were filtered using Whatman filter paper (retention size 10 µm) in heptane and cyclohexane. The products were repeatedly washed in acetone and THF and dried under vacuum.

Method 2. F127(PEO)–g–PVP, F127 (6 g), in aqueous solution (60 ml) was heated to 70 °C using an oil bath and kept at that temperature under constant stirring and nitrogen purging. At the same time, vinyl pyrrolidone (13 ml) was heated to 70 °C and transferred quickly to a 250-ml three-necked flask containing an aqueous solution of F127. Ammonium persulfate was dissolved in 2 ml of vinyl pyrrolidone and then added into the resulting solution. The reaction was kept at 70 °C under constant stirring and nitrogen purging for 6 h. After that, the solution containing the product was freeze-dried. The white powder was washed using THF and acetone and dried under vacuum.

2.3. Sample preparation

Pluronic F127–g–PVP copolymers were dissolved in distilled water under gentle stirring. The solutions were centrifuged to remove any contaminant and allowed to equilibrate for more than 24 h.

3. Characterization

3.1. Fourier transform infrared spectrometer (FTIR)

A Perkin–Elmer System 2000 Fourier transform infrared spectrometer was used to characterize the polymer. First, a background spectrum was run. The copolymer sample was then thoroughly mixed with KBr powder with careful grinding and then the mixture was pressed into pellets. The spectrum of the mixed pellet was collected against the spectrum of the background. A total of 10 scans at a resolution of 4 cm^{-1} (in the Mid IR region of 4000–400 cm^{-1}) were obtained to achieve a good signal-to-noise ratio.

3.2. Nuclear magnetic resonance (NMR)

The ^1H NMR studies were carried out on a Bruker instrument operating at 400 MHz. $CDCl_3$ was used as the solvent and TMS was used as the internal zero reference.

3.3. Differential scanning calorimetry (DSC)

Thermal studies were performed using a DSC (DSC 2920, TA Instruments, USA), equipped with a refrigerated cooling