

Synthesis and Rheological Behavior of Hydrophobically Modified Block Copolymers

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ABSTRACT: Hydrophobically modified polymers were synthesized via esterification reactions between a commercial triblock copolymer composed of ethylene oxide (EO) and propylene oxide (PO) segments (EO₂₀PO₇₀EO₂₀) and lauric and oleic acids. Rheological studies of aqueous systems containing the original copolymer and the synthesized products were performed to evaluate the effects of chemical modification, the presence of salt, and temperature on the rheology of the systems due to changes in the micellar structures. It was verified that the systems containing the synthesized products presented shear-thinning behavior even in the absence of salt. In addition, increasing the temperature and salt concentration enhanced the hydrophobic character of the poly(propylene oxide) segment and reduced the hydration of the

poly(ethylene oxide) segment; this favored the adequate packing needed to form long, wormlike micelles and resulted in pronounced shear thinning. The formation of a complex micelle structure probably occurred in the systems above the critical micellar temperature of the original copolymer because under this condition the molecules presented three alternate hydrophobic segments that had to dive into the micelle structure. The formation of long, wormlike micelles was also evidenced by the Maxwellian behavior observed in rheological oscillatory measurements. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3047–3055, 2010

Key words: micelles; rheology; structure-property relations; surfactants; synthesis

INTRODUCTION

Water-soluble triblock copolymers such as poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) are commercially available non-ionic surfactants known as Pluronics or poloxamers. Depending on the molecular weight and the poly(propylene oxide) (PPO)/poly(ethylene oxide) (PEO) ratio obtained during the synthesis of these copolymers, different applications are found for these products, such as detergency, foaming, dispersion stabilization, emulsification, drug delivery, and templating in the synthesis of structured catalysts.^{1–8}

At low temperatures, aqueous solutions of these polymers consist of unimers that self-assemble to form micelles as the temperature or concentration is increased. Therefore, a critical micellar concentration and a critical micellar temperature (CMT) can be identified.^{9–12} These parameters are commonly studied with differential scanning calorimetry^{12–17} and fluorescence or ultraviolet probe spectroscopy.^{10,18,19}

Micellization is driven by the hydrophobic nature of the PPO blocks, which will form the micellar core, whereas the hydrophilic PEO blocks will form the micellar corona.^{11,12,20} The micelles grow with temperature, and at high temperatures, near the cloud-point temperature, rod micelles may be formed.²¹

At high concentrations, some Pluronic solutions present a significant increase in the viscosity when they reach a critical temperature, at which thermoreversible gelation takes place. Below this temperature, the solution behaves as a viscous liquid with Newtonian behavior, whereas above this temperature, shear-thinning behavior is observed.^{22–26}

The effects of salts and cosolvents have been studied for copolymers such as Pluronic P123 (EO₂₀PO₇₀EO₂₀, where EO is ethylene oxide and PO is propylene oxide) and Pluronic P85 (EO₂₇PO₃₉EO₂₇), respectively. It has been verified that additives which dehydrate the micellar corona (PEO) or swell the micellar core (PPO) lead to high-viscosity aqueous systems that also exhibit shear-thinning behavior. It has been suggested that these additives change the critical packing parameter (CPP) of nonionic surfactant copolymers, in which the micelles present a sphere-to-rod transition followed by the formation of wormlike micelles.^{27–32}

In both cases (the presence of salt and cosolvents), the critical micellar concentration is strongly

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temperature-dependent because the hydrophobicity of the PPO block increases with it. This fact limits the use of Pluronics as rheology modifiers at low temperatures. For this reason, the chemical modification of Pluronics with permanent hydrophobic segments may be an interesting way of solving this problem.

Different hydrophobically modified Pluronics have been synthesized and studied, mainly with the objective of obtaining efficient drug delivery systems. Xiong et al.³³ produced an amphiphilic pentablock copolymer (PLA-F127-PLA) with Pluronic F127 and poly(lactic acid) (PLA). Polycaprolactone (PCL) has also been used to synthesize modified Pluronics (PCL-Pluronic-PCL).^{34,35} Poly(acrylic acid) (PAA) was grafted onto Pluronic F127 to produce amphiphilic F127-g-PAA graft copolymers.^{36,37} Compared with the original Pluronics, the modified copolymers can form reversible gels in water at lower concentrations and above a certain temperature.

The aim of this study was to evaluate the effects of temperature and the presence of salt on the rheological behavior of new hydrophobically modified Pluronics and to discuss how these parameters affect the micellar structures formed. In this work, the commercial triblock copolymer Pluronic P123 was hydrophobically modified through the coupling of fatty acids (FAs) on both ends of the copolymer, which led to FA-P123-FA products. The rheological properties of aqueous systems containing the products were evaluated with oscillatory and rotational measurements in a rheometer.

EXPERIMENTAL

Materials

Pluronic 123 (EO₂₀PO₇₀EO₂₀) was purchased from Aldrich (São Paulo, Brazil) and dried overnight *in vacuo* before use. The FAs, oleic acid (C18.1) and lauric acid (C12), were purchased from Vetec Química (Duque de Caxias, Brazil), in addition to toluene and *p*-toluenesulfonic acid. These technical-grade chemicals were used as received.

Synthesis and characterization of the FA-P123-FA block copolymers

FAs were attached to both ends of the Pluronic 123 copolymer to obtain amphiphilic FA-P123-FA block copolymers. The syntheses were conducted as typical esterification reactions with *p*-toluenesulfonic acid as the catalyst and toluene as the solvent. A Dean-Stark apparatus was used to remove the water that formed during the reactions through azeotropic distillation. With this procedure, the solvent (toluene) returned to the reaction medium, whereas the water remained in the Dean-Stark apparatus and shifted the chemical equilibrium to ester formation;

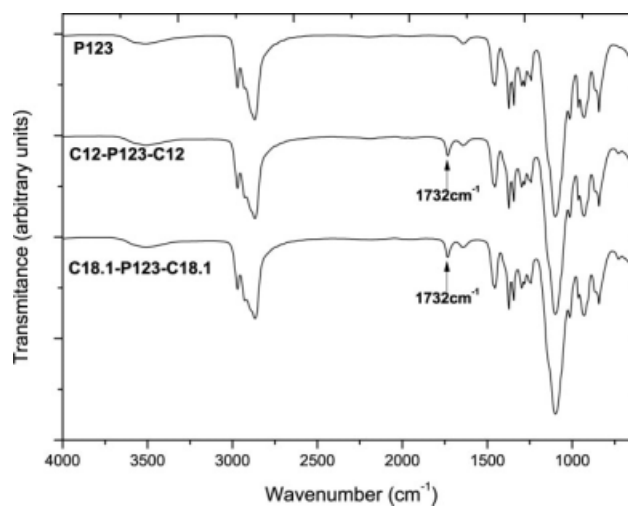


Figure 1 Infrared spectra of the original Pluronic P123 and the synthesized products C12-P123-C12 and C18.1-P123-C18.1.

this led to high yields. At the end of the reaction, when the system returned to room temperature, the products precipitated and were washed several times with toluene. The remaining solvent was removed with a rotatory evaporator. The synthesized products (FA-P123-FA) were characterized with infrared spectroscopy (Spectrum One Fourier transform infrared spectrometer, PerkinElmer, Germany) and proton nuclear magnetic resonance (¹H-NMR; 200-MHz Avance DPX-200, Bruker, Karlsruhe, Germany).

Rheology

Rheological measurements were performed with an RS1 rheometer from Haake (Karlsruhe, Germany). For high-viscosity systems, a cone-and-plate sensor was used. In rotational experiments, the shear rate was varied between 5×10^{-3} and 1000 s^{-1} . Oscillatory experiments were carried out in the same systems. The frequency was varied between 0.005 Hz and 10 Hz under a maximum stress of 1 Pa. The experiments were conducted in a frequency range in the linear viscoelastic region, as determined previously by dynamic stress sweep measurements. For low-viscosity systems, a Couette sensor was used, and in this case, only rotational experiments were performed. The shear rate was varied between 10 and 1000 s^{-1} , and the temperature was controlled with a circulating fluid bath.

RESULTS AND DISCUSSION

Characterization

The infrared spectra of the products as well as the original copolymer are shown in Figure 1. A band can be observed at 1732 cm^{-1} in the spectra of the products; this is characteristic of esters and is related

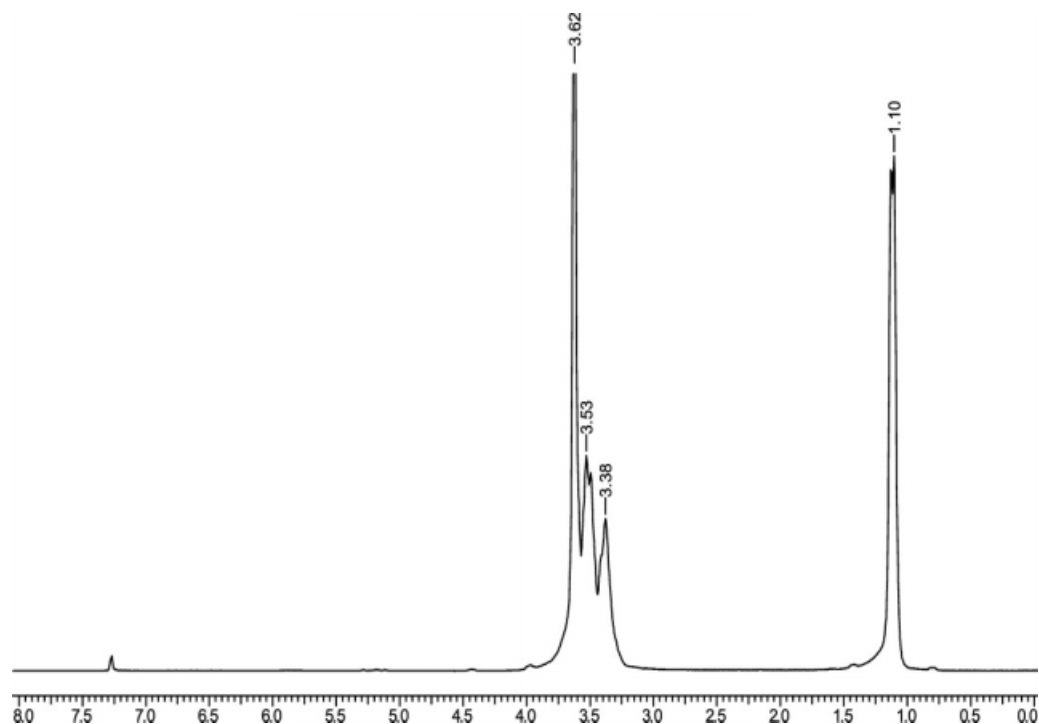


Figure 2 $^1\text{H-NMR}$ spectrum of P123 in CDCl_3 (chemical shifts in ppm).

to the stretching of the ester carbonyl. The absence of a band at 1705 cm^{-1} is also evidence of the purity of the products because unreacted FAs would have shown a band in this region due to the stretching of the acid carbonyl. Some other characteristic bands can be observed at 1100 cm^{-1} (related to stretching

vibrations of C-O-C bonds) and at 2869 cm^{-1} [related to stretching vibrations of $-\text{CH}_2-$ (symmetric and asymmetric)].

Figures 2–4 show the $^1\text{H-NMR}$ spectra of the original copolymer and the synthesized products.

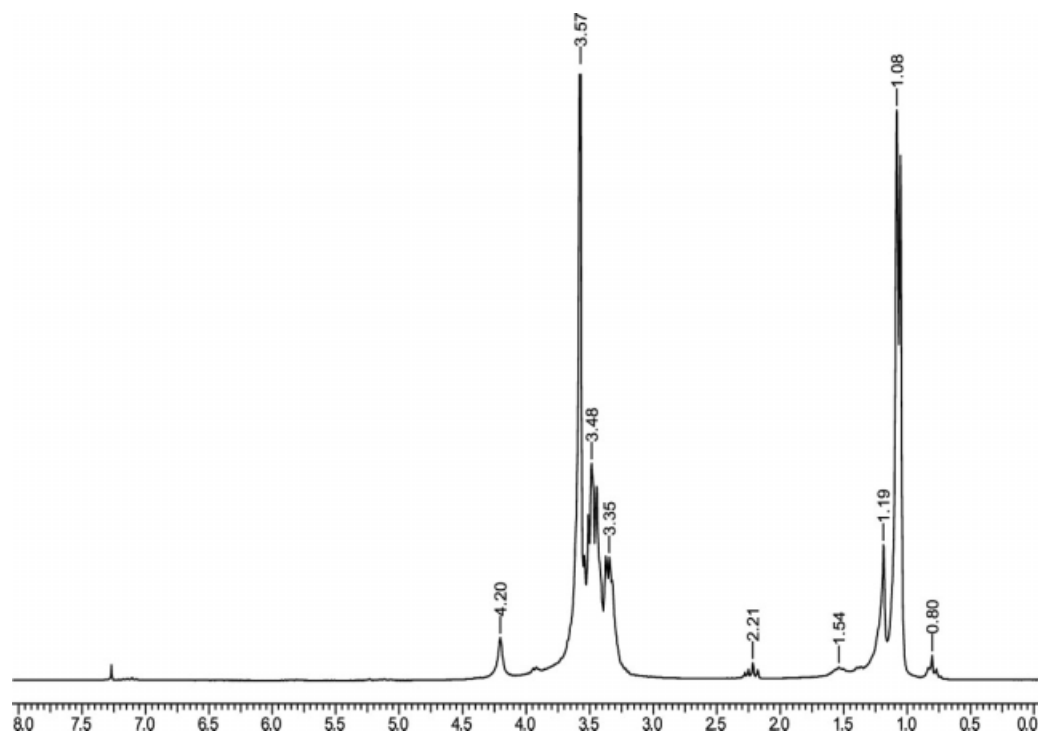


Figure 3 $^1\text{H-NMR}$ spectrum of C12-P123-C12 in CDCl_3 (chemical shifts in ppm).

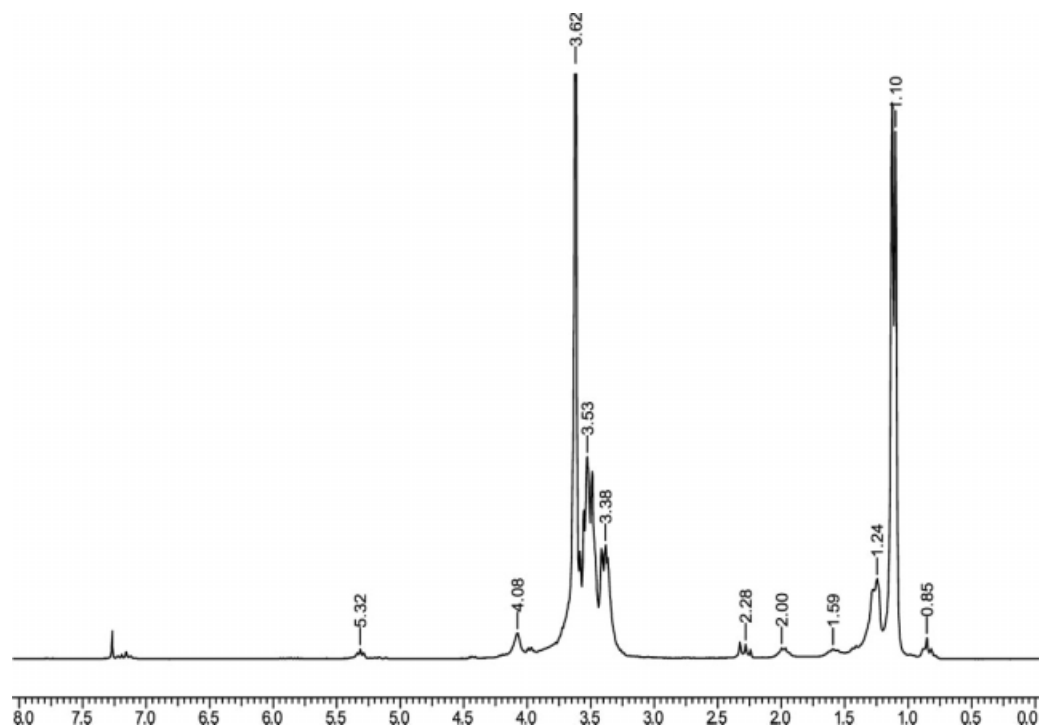


Figure 4 $^1\text{H-NMR}$ spectrum of C18.1-P123-C18.1 in CDCl_3 (chemical shifts in ppm).

$^1\text{H-NMR}$ (200 MHz, CDCl_3 , dimethyl sulfoxide, δ , ppm): 3.30–4.00 [methylene and methine groups in $-\text{OCH}_2-\text{CH}_2-$ and $-\text{OCH}_2-\text{CH}(\text{CH}_3)-$], 1.05–1.15 [methyl group in $-\text{OCH}_2-\text{CH}(\text{CH}_3)-$], 4.00–4.30 (methylene group in $-\text{CH}_2\text{OCO}-$), 2.20–2.40 (methylene group in $-\text{OCO}-\text{CH}_2-$), 1.50–1.60 (second methylene group in $-\text{OCO}-\text{CH}_2-\text{CH}_2-$), 1.17–1.30 (methylene groups surrounded by other methylene groups in the FA chains), 1.90–2.10 (methylene groups in $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$), 5.20–5.40 (methine groups in $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$), 0.70–0.90 (methyl group of the end of FA chain).

Rheology

Chemical modification effect

The influence of chemical modification on the rheological behavior of Pluronic in water at 25°C is shown in Figure 5. Newtonian behavior and a low viscosity were observed for the system that contained the original P123. However, the systems containing the hydrophobically modified polymers presented shear-thinning behavior, which was slight for C12-P123-C12 and pronounced for C18.1-P123-C18.1. It is suggested that this behavior can be explained in terms of the micelle structure in each case; a simple model, based on molecular packing, can be used. Israelachvili³⁸ defined the CPP as follows:

$$\text{CPP} = V/a_0l$$

where V is the volume of the hydrophobic portion of the surfactant, a_0 is the cross-sectional area of the surfactant head group, and l is the length of the hydrophobic segment of the surfactant. An increase in the CPP of the surfactant would promote a sphere-to-rod transition and consequent formation of wormlike micelles.³⁹ In the case of the system containing the original P123, the high hydration of the PEO segment in the Pluronic structure would significantly increase a_0 and lead to the formation of spherical micelles at 25°C ; this would result in Newtonian behavior because the individual spheres

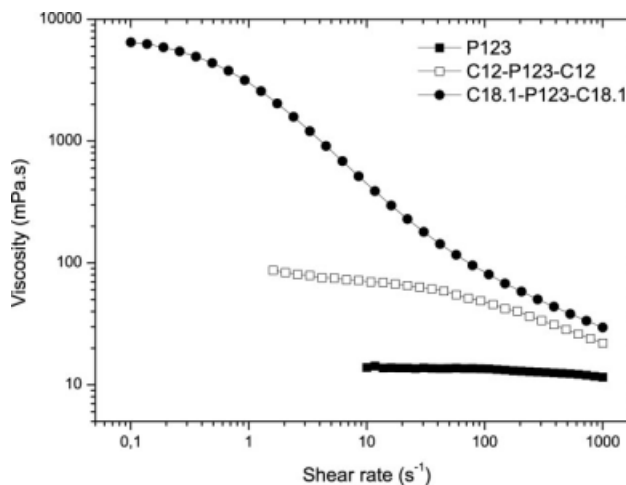


Figure 5 Shear viscosity versus the shear rate for aqueous solutions of Pluronic P123 and the synthesized products at a concentration of 20 wt % at 25°C .

contribute only a small increase to the solvent viscosity.³² In the case of the modified polymers, the coupling of the hydrophobic segments to the copolymer probably leads to a complex micelle structure in which both the PPO segment and the FA hydrocarbon chains are hydrophobic segments at 25°C. It is suggested that the FA chains contribute to a significant increase in the volume of the hydrophobic part in the micelle structure because three segments will be oriented within the micelle in a way similar to that proposed by Xiong et al.^{10,33} It is suggested that this effect would increase the CPP of the surfactant and lead to micellar growth. The increase in the zero-shear viscosity together with the observed shear-thinning behavior supports this proposal because this rheological behavior is typical of wormlike micelles.⁴⁰

Salt effect

It is known that salts such as KCl decrease the micellization temperature of Pluronics by reducing the hydration of the PPO segment in comparison with the same system in the absence of salt.³² In addition to the reduced PPO hydration, there is also a reduction in the hydration of the PEO segment. In this case, the segment remains soluble, although the effective volume of the hydrophilic segment is significantly reduced, and this will lead to the reduction of a_0 and a consequent increase in the CPP. This effect will promote the transition from spheres to wormlike micelles.³² Figure 6 shows that even the original P123 polymer may present shear-thinning behavior when an adequate amount of salt is added to the system, and this suggests the formation

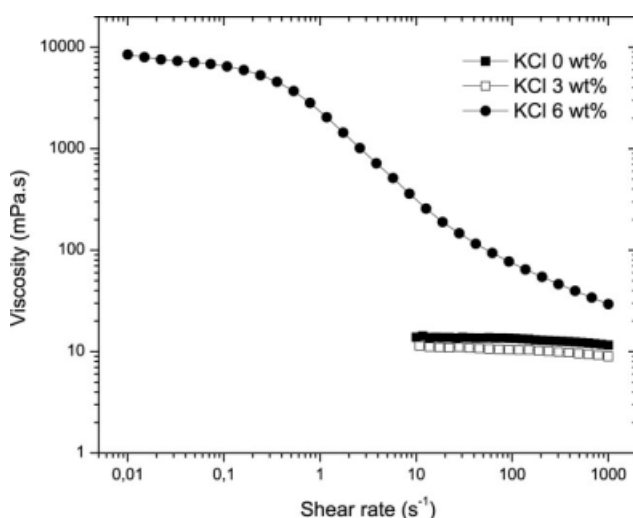


Figure 6 Shear viscosity versus the shear rate for aqueous solutions of Pluronic P123 at a concentration of 20 wt % with different KCl concentrations at 25°C.

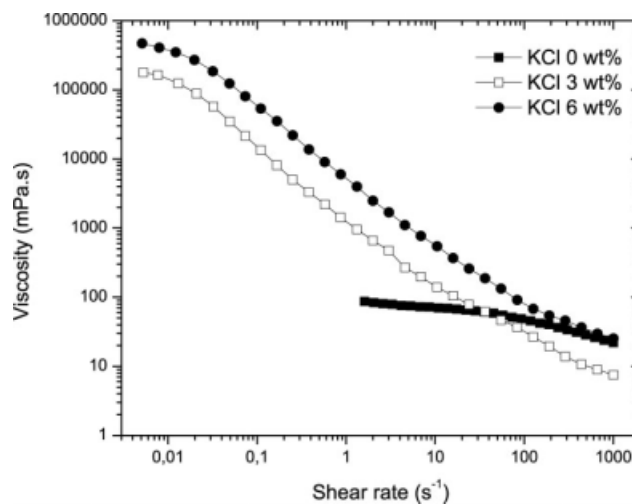


Figure 7 Shear viscosity versus the shear rate for aqueous solutions of C12-P123-C12 at a concentration of 20 wt % with different KCl concentrations at 25°C.

of wormlike micelles in systems containing KCl at 6 wt %.

The shear-thinning behavior of aqueous systems containing the modified products was enhanced with the addition of KCl, as shown in Figures 7 and 8. This effect is probably a result of the PEO segment dehydration combined with the chemical modification because both aspects would converge in an increase in the CPP due to the reduction of a_0 and the increase in V , respectively. It can also be observed that the zero-shear viscosity increased with the KCl concentration for the C12-P123-C12 systems (Fig. 7). This behavior may be a result of the enhanced dehydration effect, which led to pronounced growth of the wormlike micelles and a

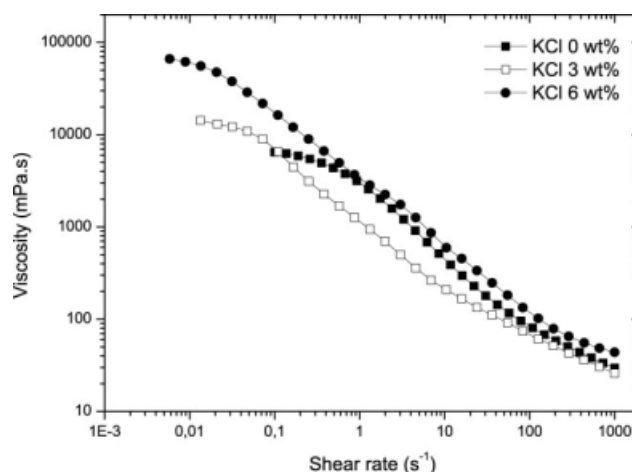


Figure 8 Shear viscosity versus the shear rate for aqueous solutions of C18.1-P123-C18.1 at a concentration of 20 wt % with different KCl concentrations at 25°C.

consequent increase in the number of entanglement points and thus resulted in higher zero-shear viscosities with the salt concentration.

The rheological behavior of the C18.1–P123–C18.1 systems at 25°C with different KCl concentrations is shown in Figure 8. Just as for the C12–P123–C12 systems, the zero-shear viscosity increased with the KCl concentration, but this effect was not so pronounced as in the first case. It is suggested that the hydrophobic chain present in C18.1–P123–C18.1 is sufficiently long to provide a significant increase in the CPP of the surfactant by increasing V , and this leads to pronounced shear thinning even in the absence of KCl. Therefore, the addition of KCl leads to only a slight increase in the viscosity of this system.

Another interesting aspect of this system is that the zero-shear viscosity values obtained with the systems containing KCl followed a trend opposite of that of the systems without the salt. The C12–P123–C12 aqueous systems with KCl presented a higher zero-shear viscosity than the equivalent C18.1–P123–C18.1 systems, but in the absence of salt, the behavior was inverted. This was probably due to the fact that in the presence of salt, the C18.1–P123–C18.1 systems were turbid, and this indicated some phase separation. With C12–P123–C12, the system with 3 wt % KCl was completely clear, and the system with 6 wt % KCl was cloudy. The longer hydrophobic chain present in the C18.1–P123–C18.1 macromolecules led to longer wormlike micelles and consequently to higher zero-shear viscosities in the clear systems. However, the resulting molecule presented a lower cloud point in comparison with C12–P123–C12, so that at room temperature and in the presence of salt, the C18.1–P123–C18.1 systems were turbid. This led to another change in the micellar structure, which prejudiced the integrity of the worm micelles and resulted in lower zero-shear viscosity values.

Temperature effect

Temperature has a singular effect on the self-assembly of Pluronic systems because the micellization process is driven by conformational changes in the polymeric surfactant chains with temperature.^{41–44} These changes enhance the hydrophobicity of the PPO segments and lead to micellization at the so-called CMT. For Pluronic P123, CMT is around 20°C, as determined by Bharatiya, through Fourier transform infrared spectroscopy, by monitoring the positions of two temperature-sensitive bands around 1080 and 1100 cm^{-1} , which are related to the stretching vibrations of C–O of PEO and PEO blocks, respectively.⁴⁵ The formation of spherical micelles above the CMT does not significantly affect the viscosity of the solution, unless the concentration of the

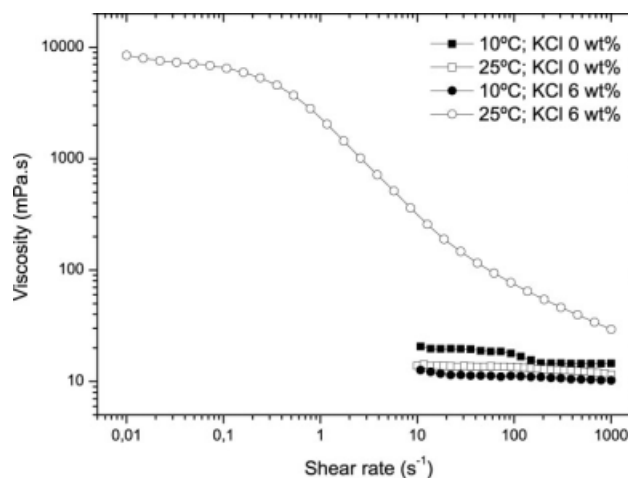


Figure 9 Shear viscosity versus the shear rate for aqueous solutions of P123 at a concentration of 20 wt % in the absence of KCl and with 6 wt % KCl at 10 and 25°C.

surfactant is sufficiently high to observe the formation of cubic mesophases, for example.⁴⁶ However, the addition of KCl to a Pluronic system above the CMT leads to the transition of spherical micelles to elongated, wormlike micelles, as shown previously (Fig. 6).

Temperature has a significant effect on the rheology of the studied systems because it is related to the polymer hydration and consequently to the packing parameter (CPP) of the molecule and the ability to form wormlike micelles.

Figure 9 presents the rheological behavior of an aqueous solution of Pluronic P123 below (10°C) and above (25°C) the CMT in the presence and absence of KCl. Without KCl, both systems behaved as Newtonian fluids, even if the structures in the solutions were micelles or unimers, as previously explained. At 10°C and in the presence of 6 wt % KCl, the system presented Newtonian behavior and a low viscosity because the polymers probably behaved as unimers at this temperature even in the presence of KCl. At 25°C, above the CMT, the addition of KCl promoted the sphere-to-worm transition and led to the observed shear-thinning behavior.

Figure 10 presents the rheological behavior of aqueous systems containing the C12–P123–C12 product. In the absence of KCl, the systems presented smooth shear-thinning behavior at 25°C and Newtonian behavior at 10°C. It is suggested that the packing parameter of the molecule is low at 10°C because the high hydration of the PEO segment at a low temperature (below the CMT of the Pluronic) would have led to an increase in the volume of the hydrophilic part of the surfactant and, consequently, the cross-sectional area of the hydrophilic segment of the surfactant (a_0). Therefore, according to the general expression for the CPP ($\text{CPP} = V/a_0$), an

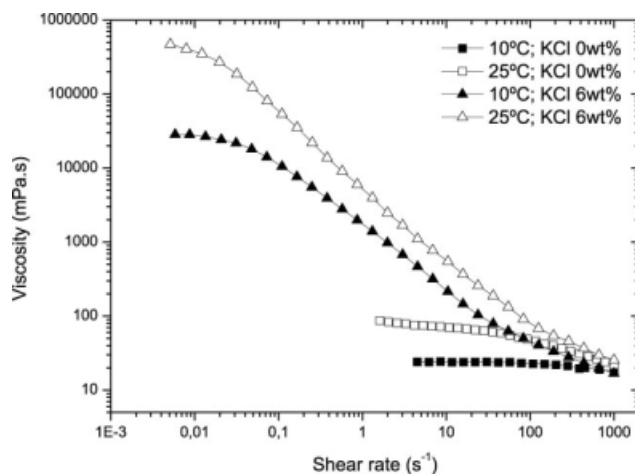


Figure 10 Shear viscosity versus the shear rate for aqueous solutions of C12-P123-C12 at a concentration of 20 wt % in the absence of KCl and with 6 wt % KCl at 10 and 25°C.

increase in a_0 would lead to a decrease in CPP and, consequently, to the formation of spherical micelles that do not contribute significantly to the viscosity of the system. At 25°C, the polymer hydration was reduced, and this reduced a_0 and increased the packing parameter. In this case, small worm micelles were probably formed because poor shear thinning was observed. In the presence of KCl, there was a pronounced increase in the viscosity of the systems below and above the CMT of the Pluronic. The dehydration effect of KCl, together with the chemical modification, probably significantly affects the packing parameter, even at a low temperature, and results in long worm micelles. These systems present a significant number of entanglement points, which result in pronounced shear-thinning behavior and high zero-shear viscosity values.

The rheological behavior of the modified Pluronic (C18.1-P123-C18.1) is shown in Figure 11. It is possible to observe that even in the absence of KCl and below the CMT of the original Pluronic, significant shear-thinning behavior was obtained. In this case, the hydrophobic chain (C18.1) was probably long enough for a packing parameter adequate for obtaining worm micelles. Thus, temperature and KCl are not critical parameters for micelle formation or for the formation of elongated micelles in this case. However, the addition of KCl to this system led to a significant increase in shear-thinning behavior above and below the Pluronic CMT. In this case, the rheological behaviors at 10 and 25°C were very similar. Although a low temperature should have increased the hydration of the polymeric chain and thus resulted in a viscosity decrease due to the decrease in the CPP and probably in the length of the worm micelles, the presence of KCl compensated for this effect, led to adequate polymeric hydration, and

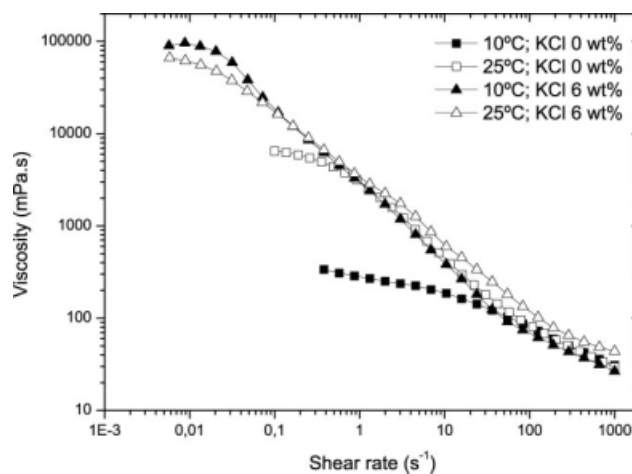


Figure 11 Shear viscosity versus the shear rate for aqueous solutions of C18.1-P123-C18.1 at a concentration of 20 wt % in the absence of KCl and with 6 wt % KCl at 10 and 25°C.

produced long worm micelles in a clear system. At 25°C, the hydration of the polymeric chains was reduced, and this led to longer worm micelles and higher zero-shear viscosities. However, the turbid system that formed led to a decrease in the shear-thinning behavior, as explained before.

Viscoelastic properties

The viscoelastic behavior of aqueous systems containing the C12-P123-C12 product is illustrated in Figures 12 and 13. At low frequencies, the loss modulus (G'') was higher than the storage modulus (G'); this characterized a viscoelastic liquid. However, at higher frequencies, G' was higher than G'' , and this was characteristic of the gel state. Figure 12 reveals that the rheology of a sample containing C12-P123-C12 at 5 wt % and KCl at 3 wt % showed Maxwellian

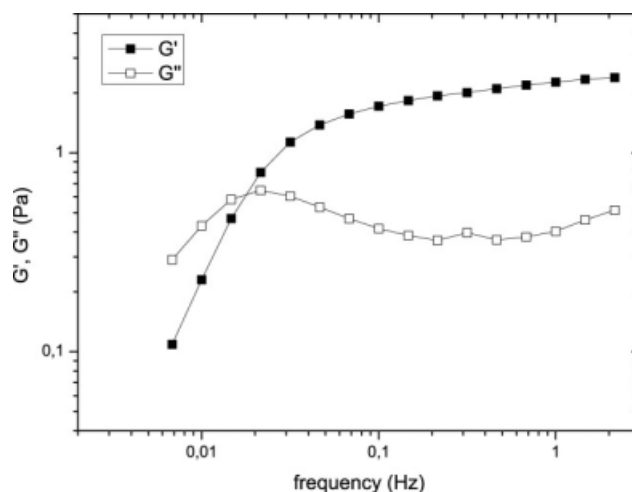


Figure 12 Viscoelastic spectra of 5 wt % C12-P123-C12 and 3 wt % KCl at 25°C.

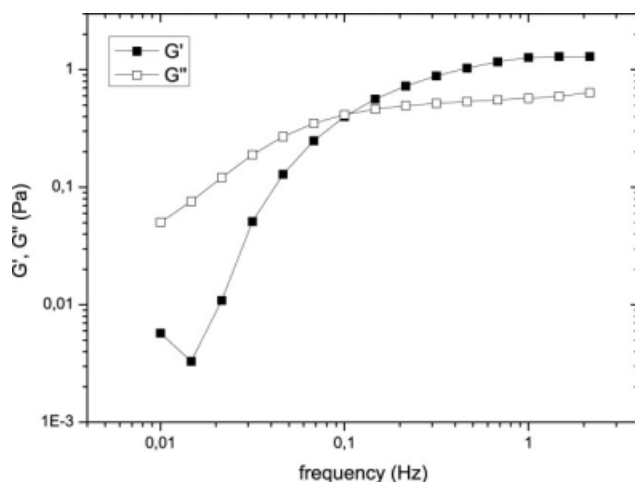


Figure 13 Viscoelastic spectra of 5 wt % C12-P123-C12 and 1 wt % KCl at 25°C.

behavior typical of systems containing wormlike micelles, in which G'' goes through a maximum and G' tends to plateau.^{47–49} The system was also characterized by a single relaxation time (t_R) in the frequency work range, which could be estimated as follows:

$$t_R = 1/2\pi f_R$$

where f_R is the frequency at which G' and G'' cross each other. Comparing the rheology profile of the sample containing C12-P123-C12 at 5 wt % and KCl at 3 wt % (Fig. 12) and the sample with KCl at 1 wt % (Fig. 13), we can observe that in the system with the higher KCl concentration, the relaxation time was longer (the crossover of G' and G'' occurred at a lower frequency). In the case of wormlike micelles, viscoelastic behavior is related to their entanglement into a transient network in a way similar to that of polymer solutions, in which the chain length is related to the number of entanglements and consequently to the relaxation time. However, wormlike micelles present a length distribution that is a function of external parameters such as salinity and temperature.⁵⁰ Therefore, it is suggested that the higher relaxation time was related to the formation of longer wormlike micelles at the higher KCl concentration, and this resulted in more entanglement points in the network; this gives support to the mechanism proposed in the Salt Effect section. Systems with higher polymer concentrations are not shown here because the crossover frequencies were too low to be accessible in the frequency range of this work, and this indicated long relaxation times.

CONCLUSIONS

The addition of KCl to aqueous solutions of P123 probably leads to a sphere-to-rod transition followed

by the formation of wormlike micelles.^{32,51} Coupling hydrophobic segments to P123 leads to systems that are able to provide shear-thinning behavior in aqueous media even in the absence of salt and at a low temperature. It is suggested that a complex micelle structure forms in the systems above the CMT of the original P123 because the molecules present three alternate hydrophobic segments that must be turned toward the center of the micelle structure. The addition of salt to these systems enhances the hydrophobic character of the PPO segment and reduces the hydration of the PEO segment; this favors the adequate packing needed to form long, wormlike micelles and leads to pronounced shear-thinning behavior and high relaxation times.

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