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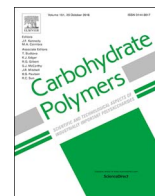
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Synthesis and characterization of carboxymethylcellulose grafted with thermoresponsive side chains of high LCST: The high temperature and high salinity self-assembly dependence

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ABSTRACT

Graft copolymers based on carboxymethylcellulose (CMC) and thermosensitive polyetheramines (ethylene oxide/propylene oxide = 33/10 and 1/9) were prepared in water, at room temperature, by using a carbodiimide and *N*-hydroxysuccinimide as activators. SLS was applied to obtain M_w , A_2 and R_g of CMC and its derivatives. Amide linkages were evidenced by FTIR and grafting percentage was determined by ¹H NMR. TGA demonstrated that copolymers were thermally more stable than their precursors. DLS, UV-vis and rheological measurements revealed that properties were salt- and thermo-responsive and linked to the polysaccharide/polyetheramine ratio and the hydrophobicity of the graft. None of the copolymers showed cloud point temperature (T_{cp}) in water, but they turned turbid in saline media when heated. Copolymers exhibited thermothickening behaviour at 60 °C (> T_{cp}) in saline media. Below their T_{cp} , they showed the ability of keeping constant viscosity or even slight increase it, which was interpreted in terms of intermolecular hydrophobic associations.

1. Introduction

In the last decades, thermoresponsive self-assembly of polymers in aqueous media has attracted much attention due to their variety of applications such as drug delivery systems (Constantin, Bucătaru, Stoica, & Fundueanu, 2017; Luo, Huang, Zhang, Xu, & Chen, 2013; Rejinold, Baby, Chennazhi, & Jayakumar, 2015), surfactants (Li et al., 2006; Wang et al., 2013), organic dye removal from water (Parasuraman, Leung, & Serpe, 2012; Parasuraman & Serpe, 2011a, 2011b) and rheological modifiers (Chen, Wang, Lu, & Feng, 2013; De Lima, Vidal, Marques, Maia, & De Balaban, 2012). A great amount of those materials consists of graft copolymers, composed by a hydrophilic backbone and thermoresponsive grafts with a lower critical solution temperature (LCST) in water. When heated, water starts to become a bad solvent to the thermoresponsive grafts, which then self-interact via intra or intermolecular associations, but macroscopic precipitation is prevented or hampered by the hydrophilic backbone, although they are very soluble at low temperatures (Bokias, Mylonas, Staikos, Bumbu, & Vasile, 2001; Cheaburu, Ciocoiu, Staikos, & Vasile, 2013; Hourdet, L'Alloret, & Audebert, 1994). Addition of salts also plays an important role on the thermo-associative behaviour, as they disturb the polymer-solvent interactions, modifying the temperature of association (Costa,

Silva, & Antunes, 2015; Heyda & Dzubiella, 2014; Kahnamouei, Zhu, Lund, Knudsen, & Nyström, 2015).

Polysaccharides are preferred as the backbone of such graft copolymers, because they combine their renewable and abundant origin, biocompatibility and biodegradability with the responsive behaviour of the grafts, turning the copolymers both thermoresponsive and environmentally friendly materials. Carboxymethylcellulose (CMC), an anionic chemically modified cellulose derivative with large water solubility, has received great attention because of their thickening, stabilizing and film-forming properties, being applied in different areas, such as cosmetics, pharmaceuticals, food, textiles, paper and oil industry (Arinaitwe & Pawlik, 2014; Azizov, Quintero, Saxton, & Sessarego, 2015; Barba, Montané, Farriol, Desbrières, & Rinaudo, 2002; D'Aloiso, Senzolo, & Azzena, 2016; Mastrantonio et al., 2015; Mondal, Yeasmin, & Rahman, 2015; Santana Fagundes, Fagundes, de Carvalho, Amorim, & Balaban, 2016). Grafting smart thermosensitive chains onto CMC backbone has proved to give very interesting properties, such as thermothickening behaviour (Aubry, Bossard, Staikos, & Bokias, 2003; Bokias et al., 2001; Marques, de Lima, & de Carvalho Balaban, 2016; Karakasyan, Lack, Brunel, Maingault, & Hourdet, 2008), faster enzymatic degradation than pure CMC (Vasile, Marinescu, Vornicu, & Staikos, 2003), gelling materials (Lü, Liu, & Ni, 2011) and

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nanocomposites for removal of heavy metal ions from aqueous media (Farag, El-Saeed, & Abdel-Raouf, 2016; Özkahraman, Acar, & Emik, 2011).

However, the above-mentioned graft copolymers have been essentially developed with low temperature responsive grafts, i.e., they have LCST values close the body temperature, targeting mainly biomedical applications. One of the limitations is that further increase in temperature to far above their LCST and higher salinity will cause the polymer precipitation due to dehydration of polymer chains and increase of intramolecular associations. Then, higher temperature responsive side chains (LCST above 40 °C) would be intended for responding to harsh environments, such as in enhanced oil recovery (EOR) at deep subterranean formations, with high temperature and salinity. Under those conditions, the polymer dissolved in water with high salinity would be able to sweep the oil to the producing well, by keeping constant viscosity or even increasing it (thermothickening behaviour) as the polymer solution experiences wide rise in temperature inside the reservoir. However, typical polymers exhibit opposite behaviour, as they decrease viscosity with increasing temperature and the salinity promotes contraction or precipitation of polyelectrolytes (Hourdet, L'Alloret, & Audebert, 1997; Wei, 2015; Wever, Picchioni, & Broekhuis, 2011).

Amino-terminated poly(ethylene oxide/propylene oxide) (PEOPPO) statistical copolymers are a family of thermoresponsive polymers known as the trademark name Jeffamine[®] (from Huntsman Corporation) (Belbekhouche et al., 2013). Differences on the ethylene oxide/propylene oxide (EO/PO) ratio drive the LCST of these polyetheramines, which can vary from below room temperature to the high temperatures of petroleum reservoirs (above 80 °C) (Azzam, Heux, Putaux, & Jean, 2010; Dulong, Mocanu, Picton, & Le Cerf, 2012; Mocanu, Mihai, Dulong, Picton, & Lecerf, 2011; Mocanu, Souguir, Picton, & Le Cerf, 2012). Interestingly, amino function at the end of the chain enables their reaction with carboxylate groups from CMC via amide linkages. In this sense, Jeffamine[®] M-2070 and Jeffamine[®] M-600 with EO/PO ratio of 33/10 and 1/9 were selected to produce novel high temperature responsive graft copolymers by grafting those polyetheramines onto CMC backbone and the thermo-associative behaviour was investigated as a function of polymer composition and addition of salts. The idea is to synthesise copolymers able to self-associate and keep constant viscosity or increase viscosity in media with high ionic strength and at the high temperatures faced at petroleum reservoirs.

2. Experimental

2.1. Materials

Sodium carboxymethylcellulose (CMC) was purchased from Sigma-Aldrich. Its weight-average molar mass of 9.0×10^4 g/mol was given by the supplier. The content of carboxyl groups was determined by ¹H NMR (Ho, 1980) and was found to be 1.00 carboxyl group per anydroglycose unit (DS = 1). Jeffamine[®] M-600 (PEOPPO600) and Jeffamine[®] M-2070 (PEOPPO2070), amino-terminated polyethers, were kindly donated by Huntsman Corporation. *N*-hydroxysuccinimide (NHS) and 1-ethyl-3-[3-(dimethylamino)-propyl]carbodiimide hydrochloride (EDC) were supplied by Carbosynth. Sodium chloride (NaCl), magnesium chloride (MgCl₂), sodium sulfate (Na₂SO₄), calcium chloride (CaCl₂), sulfuric acid (H₂SO₄), sodium hydroxide (NaOH) and deuterium oxide (D₂O) were provided from Sigma-Aldrich. Potassium carbonate (K₂CO₃) was purchased from Analar Normapur and sodium nitrate (NaNO₃) was obtained from Merck. All the compounds were used without further purification.

2.2. Synthesis of the graft copolymers

Graft copolymers were prepared by coupling reactions between CMC and the amino-terminated polyethers PEOPPO600 and

PEOPPO2070, by using EDC/NHS as condensing agents, at room temperature (~25 °C), with the stoichiometric amount to COO⁻:NH₂:NHS:EDC feed ratio of 1:2:2:4. In a reaction vessel equipped with a magnetic stirrer, 1 g of polysaccharide was dissolved under stirring in 150 mL of deionized water for at least 24 h. Jeffamine[®] was separately dissolved in 50 mL of deionized water. The solutions were mixed and subsequently diluted with 50 mL of deionized water, and the mixture was left stirring for at least 30 min. Then, the pH was adjusted to ~5 with addition of 1 M HCl. After 30 min, appropriate amounts of NHS and EDC in powder were respectively added and the reaction was left to proceed during 24 h.

The graft copolymers were purified by tangential flow filtration (TFF), using cartridge from Pall[®] with molecular weight cut-off (MWCO) of 10000 g/mol. The system was washed with 0.5 M NaCl in order to remove impurities (Hourdet et al., 1997). At various time intervals, aliquots were withdrawn from the filtrate in order to check the elimination of unreacted Jeffamine[®] by ¹H NMR spectroscopy. Finally, the system was washed with deionized water until the conductivity of the filtrate reached ~10 μS/cm⁻¹ (Marques et al., 2016), and the copolymers were recovered by freeze-drying.

2.3. ¹H NMR spectroscopy

¹H NMR spectra were obtained with a 400 MHz Bruker Avance DRX400 spectrometer in D₂O. Chemical shifts were reported in ppm and calibrated against residual solvent signal of D₂O (δ 4.8 ppm) as internal standard. Spectra were processed with ACD/NMR Processor Academic Edition software.

EO/PO ratio and molar mass of PEOPPO600 and PEOPPO2070 were determined by dissolving the samples in D₂O and analyzing at 25 °C. The peaks were integrated and then compared to the spectra found in literature (Dulong et al., 2012; Gupta et al., 2015; Hourdet et al., 1997; Mocanu et al., 2011; Park, Decatur, Lin, & Park, 2011).

The copolymers were dissolved in D₂O and analyzed at 80 °C. The integration of the characteristic peaks of PEOPPO600 and PEOPPO2070 (methyl protons) and CMC (anomeric proton of glucopyranosic unit) on the graft copolymers allowed the calculation of the experimental grafting percentage (G(%)) for each sample (Dulong et al., 2012; Mocanu et al., 2011). The grafting percentage represents average number of polyether side chains per 100 anhydroglucose units.

2.4. Infrared spectroscopy

The infrared spectroscopy was performed on a Spectrum Two™ FT-IR Spectrometer from Perkin Elmer. The solid samples (CMC, graft copolymers and CMC/PEOPPO2070 physical blend) were analyzed in KBr pellets scanning from 400 to 4000 cm⁻¹ whereas the liquid ones (PEOPPO600 and PEOPPO2070) were analyzed with an attenuated total reflectance (ATR) accessory and scanned from 1000 to 4000 cm⁻¹.

2.5. Thermal analysis

Thermal behaviour on solid state was studied by thermogravimetric analyses (TGA). The experiments were carried out on a SDT Q600 thermal analyzer, from TA Instruments, in a temperature ranging from ambient (~25) to 700 °C, with a heating rate of 10 °C/min and under nitrogen flow of 30 mL/min.

2.6. Sample preparation in aqueous media

The behaviour in solution of the polymers was investigated in different aqueous media: Milli-Q water, 0.1 M NaNO₃, 0.5 M NaCl, 0.5 M K₂CO₃ and synthetic seawater (SSW). Polymer solutions in Milli-Q water were prepared by simply adding the polymer into water and left under stirring overnight. Polymer solutions in 0.1 M NaNO₃, 0.5 M NaCl and 0.5 M K₂CO₃, were prepared by adding the macromolecules

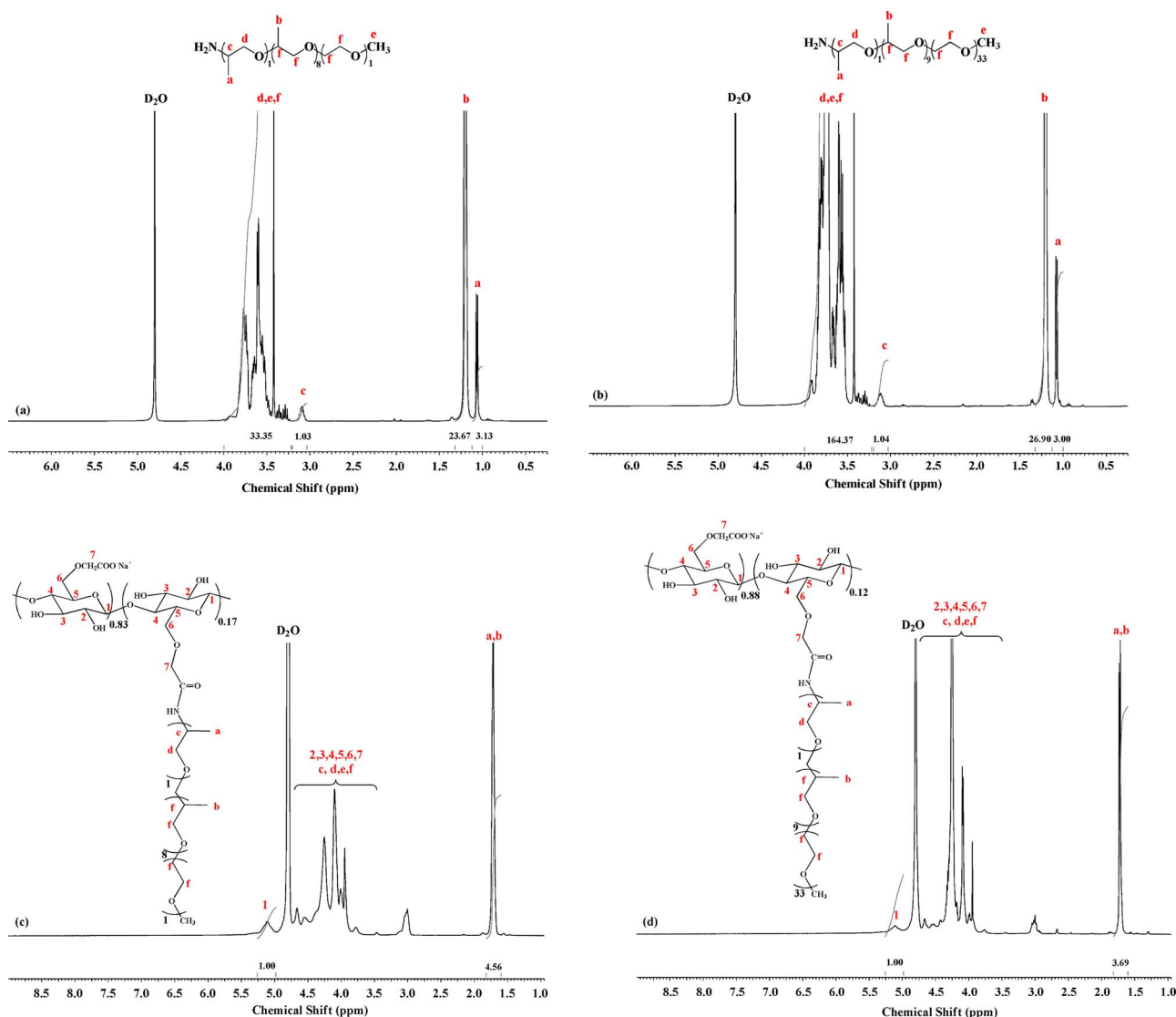


Fig. 1. ^1H NMR spectra in D_2O for (a) PEOPPO600, (b) PEOPPO2070, (c) CMC-g-PEOPPO600-17 and (d) CMC-g-PEOPPO2070-12.

into Milli-Q water and left dissolving overnight. The salts were later added to the polymer solution and left stirring for 30 min before the measurements. In all cases, the addition of salt was carried out after polymer dissolution in order to minimize the presence of aggregates (Hoogendam et al., 1998). The 0.1 M NaNO_3 , 0.5 M NaCl and the 0.5 M K_2CO_3 aqueous solutions have an ionic strength of 0.1, 0.5 and 1.5, respectively.

Synthetic seawater (SSW) was employed and prepared according to the ASTM D 1141–98 standards, aiming to observe the properties of the copolymers into a complex ionic system. The salts in a concentration higher than 1.0 g/L were applied, namely, NaCl (24.53 g/L), MgCl_2 (5.20 g/L), Na_2SO_4 (4.09 g/L) and CaCl_2 (1.16 g/L), giving an ionic strength of 0.722. Appropriate amount of copolymer was added to the SSW and left stirring overnight before measurements.

2.7. UV-vis measurements

The cloud point temperature (T_{cp}) was determined at 500 nm in a UV-vis spectrophotometer from Varian (Cary 50 Bio), equipped with a temperature controller. The system was left to equilibrate for 5 min at each temperature before measurement. The cloud point was defined as the temperature corresponding to a 50% decrease in optical transmittance (Qiu, Tanaka, & Winnik, 2007; Xu, Ye, & Liu, 2007).

2.8. Dynamic and static light scattering measurements

Dynamic light scattering (DLS) and static light scattering (SLS) experiments were performed using an ALV laser goniometer (ALV-Langen, Germany), which consists of a 35 mW red He-Ne linear polarized laser operating at a wavelength of 632.8 nm, an ALV-5004 multiple τ digital correlator with a 120 ns initial sampling time, and a temperature controller. The scattering angles ranged from 30° to 150° , with a 5° step-wise increase. The aqueous solutions of polymers were filtered directly into the glass cells through $0.45 \mu\text{m}$ MILLIPORE Millex[®] LCR filter. Data were collected using the digital ALV Correlator software.

DLS analyses were made at 25 and 60°C , and the counting time for measuring the scattering intensities was of 300 s. The relaxation time distributions, $A(t)$, were obtained using CONTIN analysis of the auto-correlation function, $C(q,t)$. The diffusion coefficient (D) was obtained from the linear dependence of the relaxation frequency ($1/\tau$) on the squared wave vector modulus (q^2). Then, the hydrodynamic radius (R_h) was calculated from D by using the Stokes-Einstein relation (Otsuka et al., 2010).

SLS measurements were performed at 25°C , and the scattering intensity of polymer solutions, at different polymer concentrations, were corrected by the 0.1 M NaNO_3 signal (solvent) and normalized by the toluene signal (calibration standard). The weight-average molecular

Table 1
Grafting percentage (G), Weight-average molar mass (M_w), radius of gyration (R_g), and the second virial coefficient (A_2) for CMC and their graft copolymers.

Sample	Grafting Percentage G (%) ^a	M_w (g mol ⁻¹) ^b	A_2 (mol.L g ⁻²) ^b	R_g (nm) ^b
CMC	–	9.0×10^4	9.1×10^{-6}	43.1
CMC-g-PEOPPO-02070-12	12	4.3×10^5	6.9×10^{-7}	68.3
CMC-g-PEOPPO600-17	17	6.0×10^5	1.7×10^{-6}	99.0

^a Determined by ¹H NMR, in D₂O, at 80 °C.

^b Obtained from static light scattering (SLS) by Zimm plot in 0.1 M NaNO₃, at 25 °C.

weight (M_w), radius of gyration (R_g), and second virial coefficient (A_2) values were estimated by Zimm plot, which was constructed by using the ALV Static & Dynamic FIT and Plot software. Refractive index increment (dn/dc) of CMC in 0.1 M NaNO₃ was established at 0.163 mg/L (Hoogendam et al., 1998; Vidal, Balaban, & Borsali, 2008) and was considered to not depend on the degree of grafting.

2.9. Rheological measurements

Rheological behaviour was verified on a Haake Mars rheometer from Thermo, equipped with a DG41 coaxial cylinder sensor. Shear rate dependence of the apparent viscosity was measured at 25 and 60 °C, controlled by a thermostatic bath coupled to the equipment. Data were collected and stored by using the RheoWin4 software.

3. Results and discussion

3.1. Synthesis and ¹H NMR characterization

Structural characterization of PEOPPO600 and PEOPPO2070 performed by ¹H NMR spectroscopy revealed peaks at 1.00–1.11 ppm from methyl protons near to amine extremity (doublet of CH₃–CHOR–NH₂); 1.11–1.32 ppm from other methyl protons of propylene oxide; 3.03–3.20 ppm due to –CH adjacent to nitrogen (Park et al., 2011); 3.22–4.00 ppm due to CH–CH₂ from propylene oxide and CH₂–CH₂ from ethylene oxide and the peak at 3.42 ppm can be attributed to methoxy protons (–O–CH₃) (Hourdet et al., 1997) (Fig. 1(a) and (b)). The integrations are equivalent to an EO/PO molar ratio of 1/9 and 33/10, with a corresponding molar mass of 597 and 2047 g/mol, for PEOPPO600 and PEOPPO2070, respectively. The results are in good agreement with the data reported by the supplier.

Due to the higher molecular weight of the polysaccharide, ¹H NMR measurements for copolymers were performed at 80 °C, in order to obtain spectra with better resolution, as exhibited in Fig. 1(c) and (d). Copolymers displayed the characteristic peaks of both CMC (anomeric proton) and polyetheramines (methyl groups) on ¹H NMR spectra. Methylene and methyne protons from PEOPPO and the protons from CMC, except the anomeric one, appeared overlapped at 3.65–4.72 ppm. Contrary to PEOPPO, the signal of the methyl group adjacent to the primary amine (doublet of CH₃–CHOR–NH₂) was superposed with the other methyl protons of PEOPPO on copolymers spectra. This downfield shift can be attributed to the amide linkage formed by the reaction between amino group from PEOPPO and COO⁻ group from CMC that deshielded the adjacent methyl protons (Park et al., 2011).

The grafting onto reactions between a backbone bearing COO⁻ groups and amino-terminated polymer chains, oligomers or small molecules has been typically accomplished with the aid of coupling agents, which activate the carboxylic groups to the nucleophilic attack of amino groups and producing amide bonds (Durand & Hourdet, 1999; Gupta et al., 2015; Lü et al., 2011; Petit, Karakasyan, Pantoustier, &

Hourdet, 2007; Wang, Iliopoulos, & Audebert, 1988). For water-soluble polymers, such as polysaccharides, peptide coupling can be easily achieved in water at acid media (pH ~5) by using the pair EDC/NHS as coupling agents, as the procedure followed in this work. In this case, it is well established that acid groups from polysaccharide react with protonated EDC forming an unstable O-acylurea that can be rearranged by NHS to a more stable activated ester intermediate, which is then converted to the graft copolymer by reaction with amino-terminated compound. Alternatively, amide linkages can also be produced by direct reaction of O-acylurea with amine or by attack of a carboxylate (COO⁻) to the O-acylurea, giving an acid anhydride, which then reacts with the amine. However, rapid hydrolysis of O-acylurea and its rearrangement to an unreactive by-product are diminished by NHS (Dulong et al., 2012; Karakasyan et al., 2008; Montalbetti & Falque, 2005; Nakajima & Ikada, 1995).

Since no phase transition was detected in water for both graft copolymers (visual tests and UV-vis), grafting percentage could be easily determined in D₂O by ¹H NMR integrations at 80 °C. Superior grafting percentage was obtained when PEOPPO600 was grafted onto CMC (Table 1), probably because of its shorter chain length, when compared to PEOPPO2070, which promotes lower steric hindrance and higher mobility on reaction medium leading to a higher grafting efficiency (Azzam et al., 2010; Hourdet et al., 1997; Xia et al., 2010). Also, it was noted that grafting percentages reached at most 17%, even with excess of reagents relative to COO⁻ groups were employed. This performance can be attributed in part due to the rearrangement of some of the O-acylurea intermediate into the more stable N-acylurea, which is unreactive towards primary amines. This behaviour decreases the amount of carboxylate groups available for grafting reaction. In fact, a signal centred at about 3.00 ppm on ¹H NMR spectra of both copolymers could be attributed to N-acylurea derivative, since it was not observed neither on CMC, PEOPPO nor on the filtrate ¹H NMR spectra, and it is compatible with typical chemical shift of hydrogen next to nitrogen (–CH–N–) of N-acylureas (Pouyani, Kuo, Harbison, & Prestwich, 1992). Similar signal is also observed on ¹H NMR spectra of carboxymethyl guar and carboxymethyl tamarin grafted with a low temperature responsive polyetheramine (Jeffamine[®] M-2005), by using EDC/NHS as coupling agents (Gupta et al., 2015). Another reason can be related to the acid pH (~5) of the coupling reactions that is below the pK_a of the amines (Cui & Van Duijneveldt, 2010), where a part of the amino groups is under acid form (–NH₃⁺), losing their nucleophilicity. However, it is important to mention that grafting percentage must be high enough to give thermothickening properties to CMC, but not too high in order to prevent precipitation (Hourdet et al., 1994). Besides, common literature presents much lower grafting percentages and then very high polymer concentration was applied to obtain thermothickening properties (Bokias et al., 2001; Karakasyan et al., 2008; Petit et al., 2007). Karakasyan et al. (2008), for example, showed that the ability of increasing viscosity by heating depends mainly on the proportion of the thermoresponsive material in the copolymer than on the dimensions of the main chain (Karakasyan et al., 2008).

3.2. SLS measurements

The weight-average molar mass (M_w), the second virial coefficient (A_2) and the radius of gyration (R_g) of unmodified CMC and CMC graft with PEOPPO600 and PEOPPO2070, were obtained in 0.1 M NaNO₃, at 25 °C, from static light scattering by Zimm plot (Table 1). The M_w found for CMC was in fully agreement with data reported by the supplier. As expected, when side chains were introduced to the polysaccharide backbone, the samples exhibited higher weight-average molar mass than CMC. The SLS analysis also showed that 0.1 M NaNO₃, which was applied as solvent to screen the electrostatic repulsions between the carboxylate groups, is a good solvent for all the samples, as demonstrated by positive A_2 values, indicating good polymer-solvent interactions. At the same time, the R_g values obtained for the copolymers

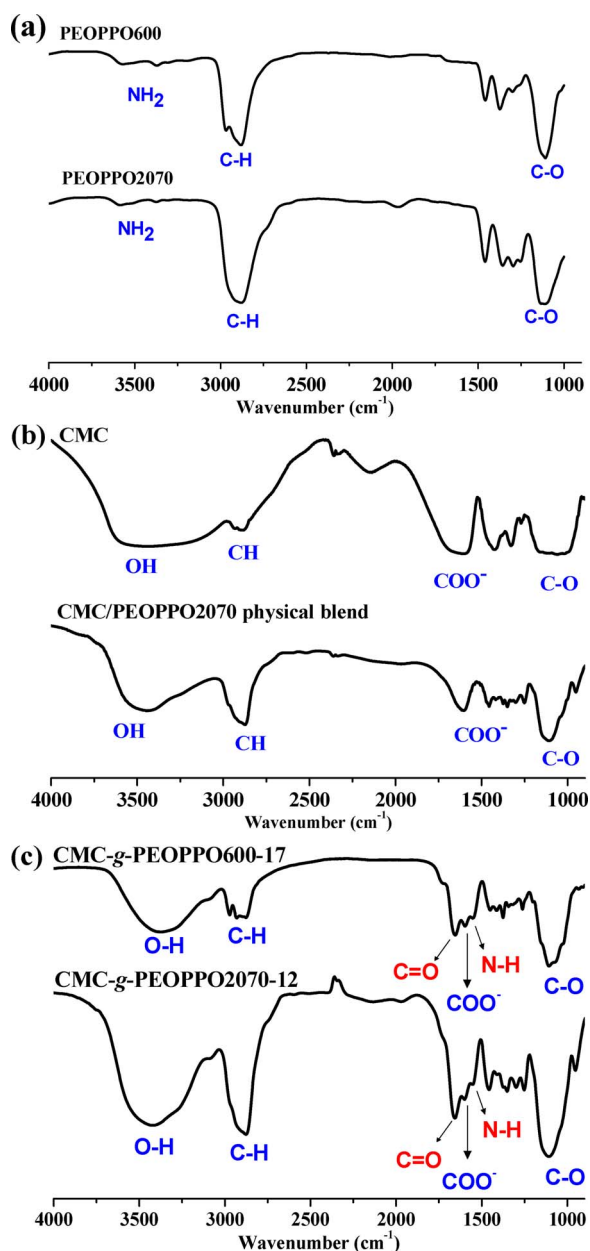


Fig. 2. Infrared spectra of (a) PEOPPO600 and PEOPPO2070, (b) CMC and CMC/PEOPPO2070 physical blend and (c) CMC-g-PEOPPO600-17 and CMC-g-PEOPPO2070-12.

were higher than the one observed for unmodified CMC, and increased with grafting percentage.

3.3. Infrared

The IR spectra of the polyetheramines are presented in Fig. 2(a). The peaks at 3630 and 3440 cm^{-1} can be related to $-\text{NH}_2$ stretching vibration, the C–H stretching vibration appeared at 2980 cm^{-1} and stretching vibration of the C–O groups at around 1100 cm^{-1} (Belbekhouche, Ali, Dulong, Picton, & Le Cerf, 2011; Dulong et al., 2012). As shown in Fig. 2(b), infrared spectrum of CMC displays a broad band centred at 3450 cm^{-1} ascribed to O–H stretching vibration, a band at 2980 cm^{-1} that can be attributed to the stretching frequency of the C–H groups and a peak at 1602 cm^{-1} due to asymmetric stretching vibration of the carboxylate groups. In addition, a peak at 1420 cm^{-1} can be assigned to both COO^- symmetric stretching vibration and $-\text{CH}_2$ scissoring and the peak at 1330 cm^{-1} can be related to the O–H bending vibration. The intense band at 1072 cm^{-1} can be

ascribed to the ether groups from the polysaccharide (Marques et al., 2016). The infrared of a physical blend of CMC and PEOPPO2070 shows a simply superposition of the peaks from CMC and the polyetheramine and no new absorptions bands appeared (Fig. 2(b)).

Infrared spectra of the copolymers (Fig. 2c) confirmed that the grafting reaction was successfully achieved due to the presence of the characteristic bands of amide I (C=O) at around 1655 cm^{-1} and of amide II (N–H) at 1550 cm^{-1} (Mocanu et al., 2011), that did not appeared neither on the physical blend nor on the precursors spectra (Fig. 2(a) and (b)). Additionally, the copolymers displayed a large band at around 3420 cm^{-1} that was attributed to O–H stretching vibrations of CMC and a band at 2920 cm^{-1} related to stretching frequency of the C–H groups from CMC and PEOPPO. The carboxylate groups were detected with asymmetric stretching vibration peaks at around 1559 cm^{-1} , and the band at around 1100 cm^{-1} , can be ascribed to both ether groups from CMC and C–O stretching frequency of the polyetheramines (Belbekhouche et al., 2011; Campana-Filho & De Britto, 2009; Dulong et al., 2012; Yadollahi & Namazi, 2013).

3.4. Thermal analysis

Fig. 3 presents the thermogravimetric curves of CMC, PEOPPO600, PEOPPO2070, CMC/PEOPPO2070 physical blend, CMC-g-PEOPPO600-17 and CMC-g-PEOPPO2070-12. CMC and graft copolymers exhibited a mass loss below 100 $^{\circ}\text{C}$, which was attributed to moisture. CMC displayed a thermal degradation process in the 250–300 $^{\circ}\text{C}$ temperature range, related to the decomposition of polysaccharides (Marques et al., 2016; H.-f. Zhang et al., 2009). PEOPPO600 and PEOPPO2070 showed a mass loss at 165–370 $^{\circ}\text{C}$ and 310–410 $^{\circ}\text{C}$ temperature range, respectively. The physical blend between CMC and PEOPPO2070 displayed a similar thermal degradation profile to that of unmodified CMC. CMC-g-PEOPPO600-17 showed a single thermal degradation step after dehydration, in the 245–395 $^{\circ}\text{C}$ temperature range, indicating that chemical modification of the polysaccharide with PEOPPO600 turned the copolymers thermally more stable than its precursors. When CMC was grafted with longer PEOPPO chains, that is CMC-g-PEOPPO2070-12, the sample displayed a two-step thermal degradation after dehydration, at 250–300 $^{\circ}\text{C}$ and 350–420 $^{\circ}\text{C}$. The first step can be attributed to the backbone and the second one to the side chains, as also exhibited by CMC-g-poly(*N*-isopropylacrylamide) graft copolymers (Bokias et al., 2001; Vasile, Bumbu, Dumitriu, & Staikos, 2004).

3.5. UV-vis measurements

Lower critical solution temperature represents the temperature at the minimum of the phase separation curve on temperature versus concentration diagram (Gil & Hudson, 2004). Its corresponding

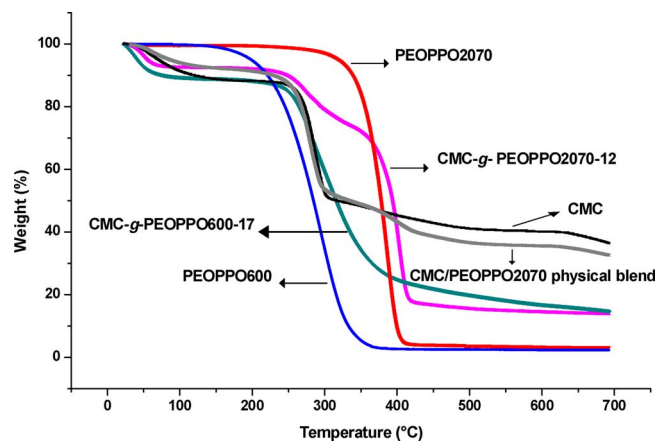


Fig. 3. TG curves of CMC, PEOPPO600, PEOPPO2070, CMC/PEOPPO2070 physical blend, CMC-g-PEOPPO600-17 and CMC-g-PEOPPO2070-12.

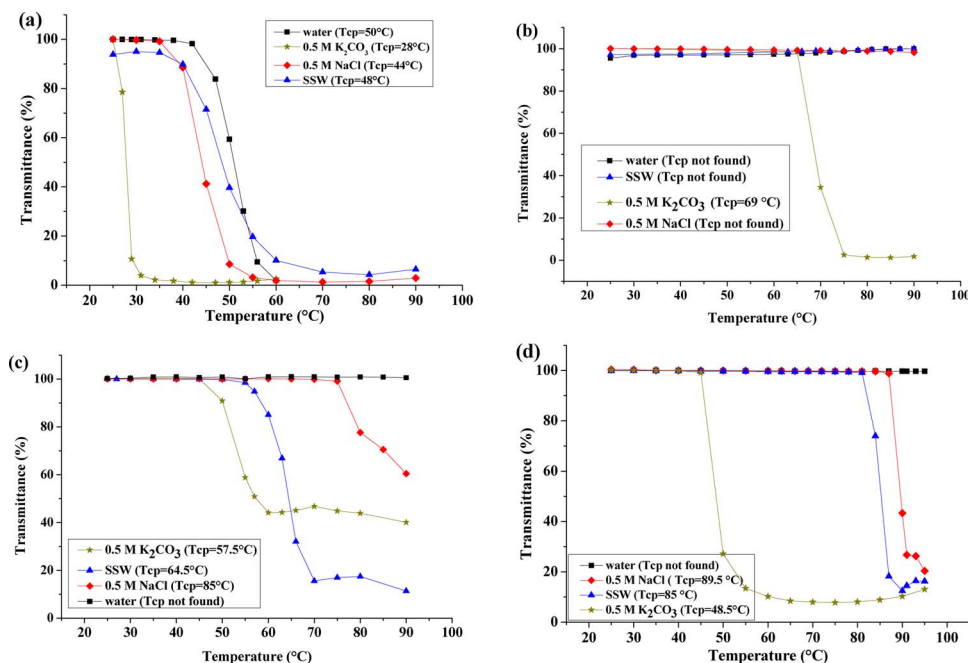


Fig. 4. Transmittance versus temperature for (a) PEOPPO600, (b) PEOPPO2070, (c) CMC-g-PEOPPO600-17 and (d) CMC-g-PEOPPO2070-12 in different aqueous media. Cloud point temperatures are indicated inside the legend.

concentration is the lower critical solution concentration (Weber, Hoogenboom, & Schubert, 2012). For practical purposes, however, commonly cloud point temperature (T_{cp}) is determined instead of LCST value, which represents the phase transition at a desired and more useful concentration (Liu, Fraylich, & Saunders, 2009; Osváth & Iván, 2017).

The cloud point temperatures and the transmittance versus temperature for PEOPPO600, PEOPPO2070 and copolymers are shown in Fig. 4. Polymer concentration of 10 g/L was chosen for the polyetheramines in order to compare it with previous determination of T_{cp} showed in literature for PEOPPO600. For graft copolymers, lower concentration was applied to get closer of more economical and representative applications. Difference between PEOPPO600 T_{cp} obtained in this work (50 °C) (Fig. 4a) and literature value (60 °C), at the same polymer concentration, might be related to the condition of analysis. For example, even by using the same technique, such as measuring transmittance versus temperature by UV-vis, differences may be obtained if the T_{cp} is defined as the onset of transmittance decrease, at 50% of decrease on transmittance, or as the point of inflection of the turbidity vs. temperature (Liu et al., 2009; Osváth & Iván, 2017).

At low temperatures, PEOPPO600 solubility may be attributed to hydrogen bonding between oxygen of the polymer chain and water molecules. At the same time, water molecules form a cage-like structure around the hydrophobic portions of the polyetheramine. Rising temperature provides energy to progressively dislocate the water molecules around the polymer and promotes polymer–polymer hydrophobic interactions as well as intramolecular solvent–solvent and polymer–polymer hydrogen bonding, leading to phase transition (Cho, Lee, & Cho, 2003; Deshmukh, Sankaranarayanan, Suthar, & Mancini, 2012; Kříž & Dybal, 2010).

PEOPPO600 displayed lower T_{cp} in the presence of salts than in water, due to the salting out effect. Therefore, the polymer–solvent attractive interactions are reduced either by direct interaction of the ions with the hydrophilic portions of the polyether or by ion interactions with the water of hydration of PEOPPO600, reducing solvation of the polymer by water molecules (Deyerle & Zhang, 2011; Hofmann & Schönhoff, 2009; Hourdet et al., 1994). Despite the slightly higher T_{cp} in SSW than in 0.5 M NaCl, PEOPPO600 exhibited a lower transmittance in SSW already at 25 °C, which demonstrates that this polyetheramine starts to self-associate at room temperature.

On the other hand, PEOPPO2070 did not exhibited T_{cp} neither in water, 0.5 M NaCl nor on SSW, due to its higher hydrophilic ratio (EO/PO = 33/10) when compared to PEOPPO600 (EO/PO = 1/9) (Fig. 4b). However, this more hydrophilic polyetheramine showed T_{cp} of 69 °C in 0.5 M K₂CO₃, probably because it is the medium with the highest ionic strength. In addition, CO₃²⁻ is one of the anions on the Hofmeister series with better ability to decrease polymer–solvent interactions (kosmotrope). This behaviour is similar to the one found in literature for poly(ethylene oxide), which has no cloud point in water when the molar mass is lower than 2000 g/mol, but an increase in molar mass and/or addition of salts can reduce it to values lower than 100 °C (Fuchs, Hussain, Amado, Busse, & Kressler, 2015; Hourdet et al., 1994). The salt's ability depends on their type (kosmotrope or chaotrope) and concentration (de Vos, Möller, Visscher, & Mijnlief, 1994).

None of the graft copolymers showed T_{cp} in water, indicating that the charges in the stiff backbone hinder the interactions among PEOPPO side chains and additionally increase the hydrophilicity of the copolymers when compared to PEOPPO. In the presence of salts, however, an interesting salt-dependent thermosensitivity appeared. The copolymers turned turbid in all tested saline solutions, with a decrease on T_{cp} values with increasing of the medium ionic strength. It occurred, probably, as a function of the screening of the charges of the backbone combined to the salting out effect, enabling side chains to interact more easily (Fig. 4c and d).

At 0.5 M NaCl and SSW, CMC-g-PEOPPO600-17 showed lower T_{cp} than CMC-g-PEOPPO2070-12, probably because CMC-g-PEOPPO600-17 has a higher hydrophobic character and, therefore, is more salt sensitive. In 0.5 M K₂CO₃ however, an opposite behaviour appears, as the copolymer with higher HLB exhibited the lower cloud point temperature. In this case, it is assumed that CO₃²⁻ acts by interacting with the hydrophilic portions of the side chains, leading to a lower solvation of CMC-g-PEOPPO2070-12 by water molecules (Deyerle & Zhang, 2011; Zhang, Furryk, Bergbreiter, & Cremer, 2005).

3.6. DLS measurements

Dynamic light scattering measurements were performed in order to investigate the double salt and temperature effect on the hydrodynamic radius (R_h) of the responsive macromolecules (Table 2). The concentration of 1.5 g/L was selected to evaluate if the associative

Table 2
Hydrodynamic radii (R_h) for copolymers in water, 0.5 M NaCl, 0.5 M K_2CO_3 and SSW, at 25 and 60 °C.

Solvent	Polymer concentration (g/L)	CMC-g-PEOPPO2070-12		CMC-g-PEOPPO600-17	
		R_h (nm)		R_h (nm)	
		25 °C	60 °C	25 °C	60 °C
water	1.5	129	108	155	144
0.5 M NaCl	1.5	26	17 ^a ; 54 ^b	13	22.6
0.5 M K_2CO_3	1.5	18	–	14	–
SSW	1.5	28	27.6	13 ^a ; 98 ^b	48
	5.0	13 ^a ; 108 ^b	19 ^a ; 126 ^b	12.6 ^a ; 181 ^b	14 ^a ; 114 ^b

^a fast relaxation mode.

^b slow relaxation mode.

behaviour was noticeable even at a low polymer concentration. Still, the properties were also studied at 5 g/L on the more complex saline medium, the synthetic seawater. Multiangle measurements were performed in order to observe the diffusive motion of the macromolecules, providing a more accurate determination of the apparent diffusion coefficient (D), as illustrated for CMC-g-PEOPPO600-17 in Fig. 5. Relaxation modes that exhibited straight proportional dependence of relaxation frequency ($\Gamma = \tau^{-1}$) on the square wave vector modulus (q^2) were presented and indicated the translational diffusive motion of the macromolecules (Mkedder et al., 2013; Zepon et al., 2015).

Graft copolymers exhibited higher R_h in water than in saline media, probably because of the repulsion of the negative charges on the backbone and the existence of polymer–polymer intermolecular hydrogen bonding that increases the volume occupied by the macromolecules in the medium (Vidal et al., 2008). The higher the M_w , the higher the mean diameter ($2 \cdot R_h$) of the macromolecules, as a direct consequence of its lower diffusion coefficient. The mean diameter of copolymers in water was decreased when the system was heated from 25 to 60 °C, probably because of the increase on the Brownian movement that increases the diffusion coefficient of the macromolecules. The relaxation process in the presence of salts occurred at shorter time than in water, resulting in a shrinkage of the copolymers. This behaviour can be related to the screening of the charges in the backbone combined to the shrinkage of the thermosensitive grafts due to the salting out effect (Fig. S1).

Both copolymers showed unimodal relaxation time distribution at 25 °C in 0.5 M NaCl. The higher diameter of CMC-g-PEOPPO2070-12 ($2 \cdot R_h = 52$ nm) in relation to CMC-g-PEOPPO600-17 ($2 \cdot R_h = 26$ nm) can be attributed to the lower hydrophobic character of CMC-g-PEOPPO2070-12, that means, lower graft percentage and higher hydrophilic/hydrophobic ratio of PEOPPO, which promotes lower contraction of the copolymer in saline medium. Bimodal relaxation time distribution corresponding to the mean diameter of 34 and 108 nm were observed when CMC-g-PEOPPO2070-12 was heated to 60 °C in

0.5 M NaCl. The fast mode can be attributed to the shrinkage of the free macromolecules due to intramolecular associations with heating. The slow mode can be ascribed to intermolecular associations. On the other hand, CMC-g-PEOPPO600-17 exhibited one diffusion mode at both 25 and 60 °C. The mean diameter increased with temperature probably because of intermolecular associations. Even if those systems did not cloud when heated from 25 to 60 °C, intermolecular associations arise, as PPO units are able to form micelles with increasing temperature before a cloud point temperature appears (Deyerle & Zhang, 2011)

In 0.5 M potassium carbonate, both copolymers showed unimodal distributions of relaxation time at 25 °C. The macromolecules were greatly contracted, due to the highest medium salinity. When heated to 60 °C, however, both copolymers exhibited strong opalescence and the size distributions obtained were not reliable due to excessive amount of light dispersed by the samples (Larrañeta & Isasi, 2013).

Two different diffusion modes were observed in the relaxation time distribution of CMC-g-PEOPPO600-17 in SSW, at 25 °C. The fast one ($2 \cdot R_h = 26$ nm) can be related to contracted free polymer chains. Whereas the slow mode ($2 \cdot R_h = 196$ nm) can be attributed to intermolecular complexation of backbones promoted by interactions of divalent cations (Mg^{2+} and Ca^{2+}) and carboxylate groups from CMC (Vidal et al., 2008) combined to PPO intermolecular associations, in order to protect the grafts from the polarity of the medium with high ionic strength. When heated to a temperature close to its T_{cp} , only one relaxation time distribution appeared, with a mean diameter of 96 nm. In this case, bimodal to unimodal relaxation time distribution change can be ascribed to the simultaneous dehydration of aggregates and intermolecular hydrophobic associations of the former free chains, as the medium becomes gradually a bad solvent for CMC-g-PEOPPO600-17.

However, the copolymer CMC-g-PEOPPO2070-12 in SSW exhibited unimodal distributions of relaxation times at both temperatures with corresponding mean diameter of 56 and 55.2 nm at 25 and 60 °C, respectively. The slightly contraction of CMC-g-PEOPPO2070-12, at 1.5 g/L, in synthetic sea water when heated from 25 to 60 °C indicates that its higher hydrophilic character promotes higher stability under those conditions of temperature and salinity.

The increase of polymer concentration from 1.5 g/L to 5 g/L in SSW triggered aggregates for both copolymers at 25 °C, with two diffusive modes in the relaxation time distribution. The fast mode observed for CMC-g-PEOPPO600-17 was just about the same size as the one at 1.5 g/L, whereas the slow mode practically doubled its sized, due to the proximity of macromolecules on a higher concentration medium, which enables greater intermolecular associations. Rise in temperature, however, induced a contraction of aggregates and minor increase on the size of free chains (Fig. S2). In fact, this behaviour is similar to one anticipated at 1.5 g/L, where the dehydration of aggregates and intermolecular association of the former free chains are expected to occur, as the system is heated to a temperature close to copolymer T_{cp} . CMC-g-PEOPPO2070-12, in contrast, showed an increase on the mean diameter of its free chains and aggregates with increasing temperature, which can contribute to keep the thickening properties at elevated

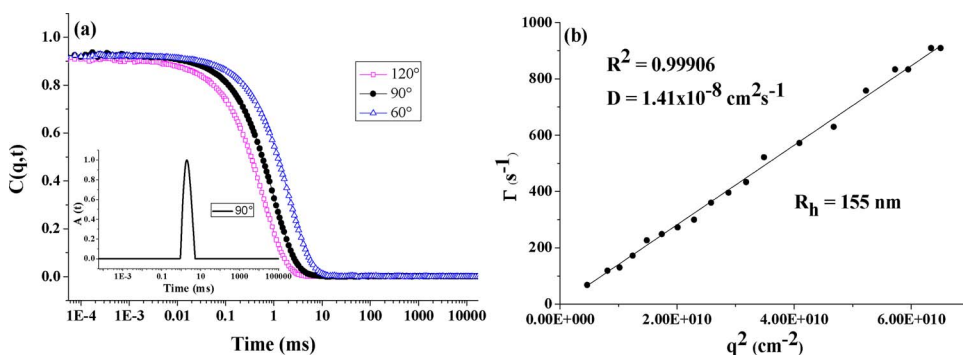


Fig. 5. (a) Autocorrelation function at different angles for CMC-g-PEOPPO600-17 in water with the respective relaxation time distribution at 90° (insert) and (b) dependence of relaxation frequency on the squared wave vector modulus (q^2).

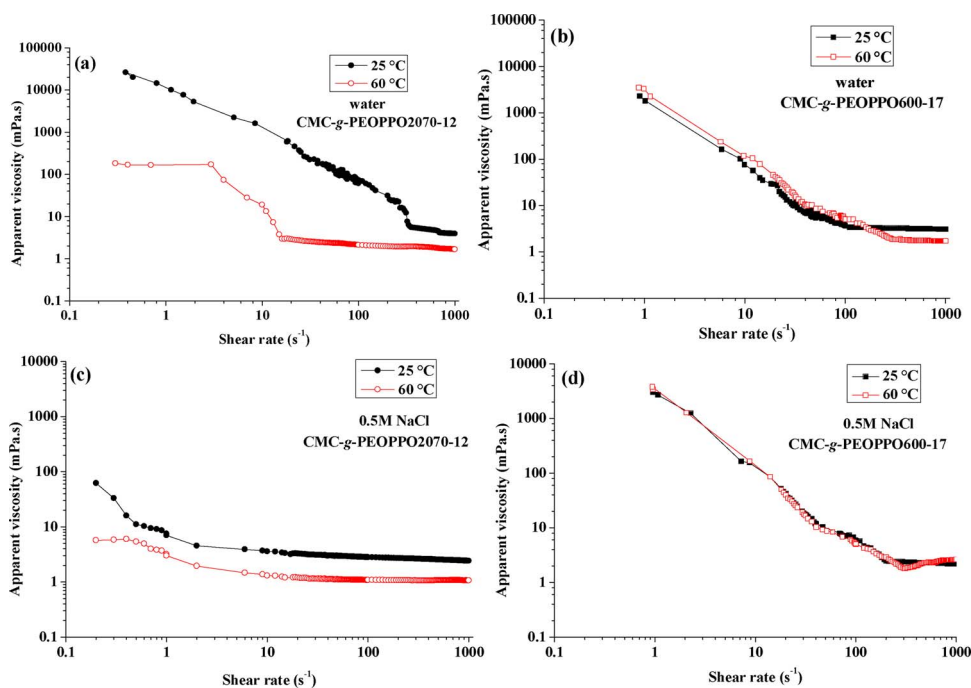


Fig. 6. Influence of temperature on the shear rate dependence of the apparent viscosity for CMC-g-PEOPPO2070-12 (round symbols) and CMC-g-PEOPPO17 (square symbols) at different aqueous media: (a and b) water, (c and d) 0.5 M NaCl, (e and f) SSW and (g and h) 0.5 M K_2CO_3 .

temperatures.

3.7. Rheology

Rheological behaviour in different aqueous media (water, 0.5 M NaCl, SSW and 0.5 M K_2CO_3) and temperatures (25 and 60 °C) was evaluated for CMC-g-PEOPPO600-17 and CMC-g-PEOPPO2070-12, at a polymer concentration of 5 g/L (Fig. 6). For all solvents and temperatures, copolymers displayed pseudoplastic behaviour, that is, apparent viscosity decreases with increasing shear rate. This behaviour occurs as a function of the disruption of entanglements and associations and orientation of macromolecules in the flow direction. At the lowest and the

highest shear rates, some systems exhibited the called first and second Newtonian ranges, respectively, in which viscosity kept unchanged with shear rate. At the first Newtonian plateau, shear rate is not enough neither to disrupt polymer–polymer interactions nor to override the random movement of the chains, and at the second plateau, macromolecules are fully aligned in the flow direction (Schramm, 2006).

In water, a rise in temperature promoted a decrease on apparent viscosity for CMC-g-PEOPPO2070-12, because of the increase on the mobility of the macromolecules (Fig. 6a). CMC-g-PEOPPO600-17, however, showed a subtle therothickening behaviour until 200 s^{-1} , from which a plateau appears and the viscosity at 60 °C turns lower than the one at 25 °C (Fig. 6b). This result indicates that, in water,

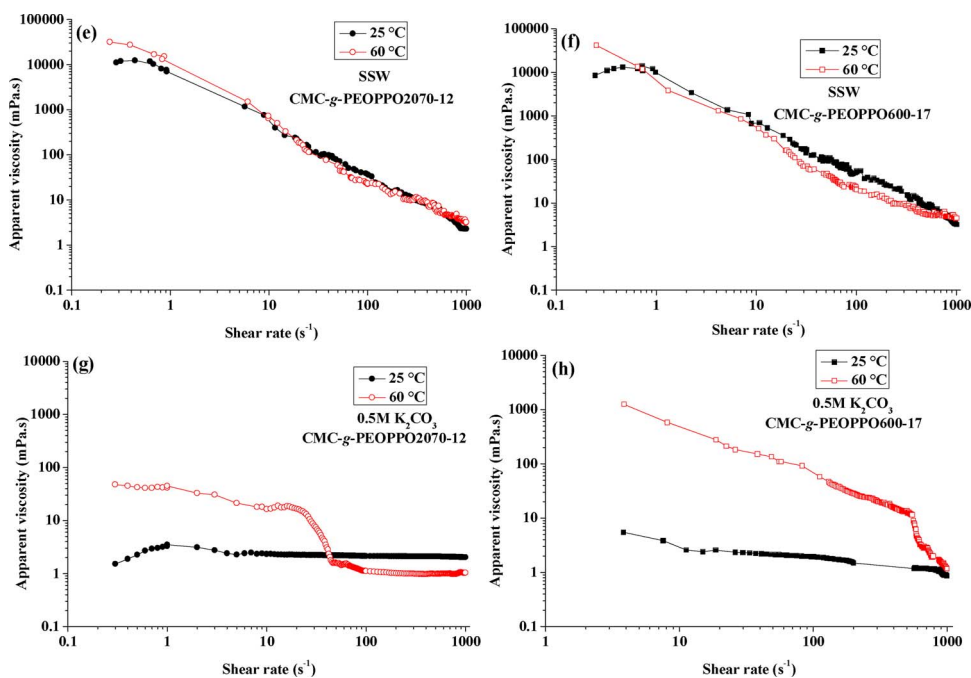


Fig. 6. (continued)

intermolecular associations are more effective the higher the grafting percentage and the lower the hydrophilic/hydrophobic ratio of the side chains. In addition, those polymer associations are improved with heating for CMC-g-PEOPPO600-17 and only higher shear rates (above 200 s^{-1}) are able to disrupt the polymer–polymer interactions and orient macromolecules parallel to the driving force.

CMC-g-PEOPPO2070–12 showed lower viscosity in 0.5 M NaCl (Fig. 6c) than in water (Fig. 6a) at both 25 and 60 °C. This behaviour can be attributed to screening of the charges from CMC and contraction of the chains caused by the salt in the medium. Heating to 60 °C caused a further decrease on viscosity, but less effectively than in water. In this case, thermally induced aggregates (detected even at 1.5 g/L– Table 4) contribute to the reduction in viscosity to be less important. CMC-g-PEOPPO600-17 in 0.5 M NaCl, on the other hand, exhibited high viscosity values, similar to its behaviour in water. However, in this case, viscosity curves at 25 and 60 °C were superposed (Fig. 6d). This suggests that hydrophobic associations induced aggregates even at low temperatures, at this polymer concentration, which contributes to the viscosity.

In SSW, with additional increase of the ionic strength, CMC-g-PEOPPO2070–12 exhibited slight superior viscosity at 60 °C than at 25 °C (Fig. 6e), at low shear rates, which agrees with the thermally induced increase of R_h of the populations detected by DLS; the higher the size of polymer chains and aggregates, the higher the viscosity of its solutions. Curves at 25 and 60 °C were superposed, as some of intermolecular interactions are disrupted with further increase of shear rate. Under the same conditions, CMC-g-PEOPPO600-17 (Fig. 6f) showed a small reduction on the viscosity with heating, as the populations shrunk when the temperature was increased (Table 2).

In 0.5 M K_2CO_3 , at 25 °C, the viscosity was the lowest when compared to the other aqueous media studied, probably because of the ability of CO_3^{2-} to decrease polymer-solvent interactions and the greater contraction of the chains on the higher salinity environment. However, rise in temperature to 60 °C, that is, above the T_{cp} for both copolymers, triggered an increase in viscosity (Fig. 6g and h). This behaviour is typical of thermothickening systems, in which there is thermally induced formation of a physical network (Aubry et al., 2003; Bokias et al., 2001).

4. Conclusion

Novel graft copolymers based on carboxymethylcellulose as the backbone and polyetheramines Jeffamine® M-2070 (PEOPPO2070) and Jeffamine® M-600 (PEOPPO600) as grafts were successfully prepared in water by using EDC/NHS as coupling agents. Amide linkages formed through the reaction between $-\text{COO}^-$ groups from CMC units and $-\text{NH}_2$ groups from PEOPPO chains were detected by IR spectroscopy. ^1H NMR integrations revealed higher grafting percentage for PEOPPO600 than for PEOPPO2070 derivative under the same conditions of reaction. Thermal behaviour on solid state showed that graft copolymers were thermally more stable than their precursors. When heated in different aqueous media, self-assembly changed as a function of temperature and salinity of the medium and copolymer composition. In the absence of salt, none of the copolymers showed cloud point temperature (T_{cp}). However, they revealed a salt dependent-thermosensitive character: the higher the ionic strength the lower the T_{cp} . They displayed thermothickening behaviour when heated from 25 to 60 °C, above their T_{cp} in 0.5 M K_2CO_3 . Even below T_{cp} , hydrophobic intermolecular associations promoted a slight increase or constant viscosity when temperature was increased from 25 to 60 °C, depending on the copolymer composition and the aqueous medium. Their high temperature and salinity self-assembly dependence reveals their potential use in harsh environments such as in deep petroleum reservoirs for enhanced oil recovery applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.carbpol.2017.12.053>.

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