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Hydrogen bonds in blends of poly(N-isopropylacrylamide), poly(N-ethylacrylamide) homopolymers, and carboxymethyl cellulose

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Abstract: Recently, it was reported that the physical cross-linking exhibited by some biopolymers could provide multiple benefits to biomedical applications. In particular, grafting thermoresponsive polymers onto biopolymers may enhance the degradability or offer other features, as thermothickening behavior. Thus, different interactions will affect the different hydrogen bonds and interactions from the physical cross-linking of CMC, the lower critical solution temperatures (LCSTs), and the presence of the ions. This work focuses on the study of blends composed of poly(N-isopropylacrylamide), poly(N-ethylacrylamide), and carboxymethyl cellulose in water and water/methanol. The molecular features, the thermoresponsive behavior, and gelation phenomena are deeply studied. The ratio defined by both homopolymers will alter the final properties and the gelation of the final structures, showing that the presence of the hydrophilic groups modifies the number and contributions of the diverse hydrogen bonds.

Keywords: Physical cross-linking; lower critical solution temperature; cononsolvency phenomenon; hydrogen bonds.

Introduction

The study of the physical cross-linking exhibited by grafting smart thermosensitive structures is growing due to the multiple benefits which could be obtained for many applications, as gelling polymers, materials for removal of heavy metals or degradation agent [1-4]. Some studies were performed using carboxymethylcellulose (CMC) due to its frequent use as viscosity modifier and stabilizer, which is used for many applications in cosmetics, food, or pharmaceutical industries. It has observed that the viscosity of Na-CMC increased when glycerin was added [5]. Later, a phenomena of gelation and/or changes in viscosity was explained by the physical cross-linking of hydrogen bonds [6], which were studied in CMC solutions prepared by mixtures of glycol/water and

poly(vinyl alcohol)/water. [7,8,1]. Intrinsic viscosity results of solutions of Na-CMC in ethylene glycol/water and methanol/water mixtures were also analyzed[9,10].

Grafting thermoresponsive polymers onto CMC led to thermothickening behavior [11-14], or better degradability properties [15]. Furthermore, these structures showed good characteristics as nanocomposites for treating wastewater, especially indicated for removing metal ions [16]. Nevertheless, some problems were found due to the high salinity, which promotes the precipitation of the polymeric chains. The use of thermoresponsive polymers as poly(*N*-ethyl acrylamide) (PNEAM), where the lower critical solution temperature is above 40 °C, could diminish this effect.

The thermoresponsive polymers can undergo the cononsolvency phenomenon in some mixtures of solvents, i.e., a volume phase transition is observed. In general, these studies were focused on poly(*N*-isopropylacrylamide) (PNIPAM), where various parameters as density, hydrophobic interactions, or chain lengths were associated with the cononsolvency phenomenon [17-20]. The PNIPAM testified this effect in mixtures of water with methanol or ethanol, among others [21-30]. The effect of monomer compositions were studied in copolymers based on *N*-isopropylacrylamide and *N*-ethyl acrylamide, where it was observed that hydrophobic polymers show a better cononsolvency behavior than hydrophilic ones [17,31].

There are many questions around the different hydrogen bonds associated with the lower critical solution temperature, the physical cross-linking, and the cononsolvency phenomenon that needs to be addressed. This work tries to identify the contributions of these parameters over the phase transition temperature and the gelation in blends based on poly(*N*-isopropylacrylamide), poly(*N*-ethylacrylamide) homopolymers and carboxymethyl cellulose in water, and mixtures of water and methanol. The thermoresponsive behavior and properties were studied by UV-vis spectroscopy, dynamic light scattering, and rheology. The results were compared with the molecular characteristics of structures.

Experimental

Materials

The monomers were purified before synthesis, where *N*-isopropylacrylamide (NIPAM, 98%, Xiya Reagent, Shandong, China) was recrystallized using *n*-hexane and toluene (9:1), and *N*-ethylacrylamide (NEAM, 99%, Aldrich, City of Saint Louis, U.S.A.) through an alumina column. Azobisisobutyronitrile (AIBN, Aldrich, City of Saint Louis, U.S.A.) was selected as initiator and was recrystallized. Sodium carboxymethyl cellulose (CMC, Macklin, Shanghai, China), deionized water (Millipore Elix 5^{UV} Millipore Corporation, Billerica, U.S.A.), diethyl ether (99.5%, Lingfeng, Shanghai, China), and methanol (MeOH, 99.5%, Damao chemical reagent, Tianjin, China) were used as received. *N,N*-Dimethylformamide (DMF, 99.5%, Macklin, Shanghai, China) was treated with nitrogen gas to remove the oxygen of the solvent.

Synthesis of homopolymers

The homopolymers were synthesized following the next steps. First, poly(*N*-isopropylacrylamide) (PNIPAM) and poly(*N*-ethyl acrylamide) (PNEAM) were prepared using specific amounts (Table 1) of monomers (NIPAM and NEAM, respectively) and initiator (AIBN), and using DMF as a solvent. Inert conditions were established for reactants placed inside of two Schlenk tubes. Then, both Schlenk tubes were placed in a thermostatic bath at 75 °C for 18 hours.

Table 1. Preparation of homopolymers.

Name	NIPAM (mol)	NEAM (mol)	AIBN (mol)	DMF (mL)
pNIPAM	0.022	--	6E-04	15
pNEAM	--	0.028	6E-04	14

Different amounts of pNIPAM and pNEAM were mixed, varying the ratio between homopolymers as is indicated in Table 2, and keeping the inert conditions. The reactions were stopped by cryogenization using liquid nitrogen. The new structures were precipitated in diethyl ether, purified twice, and dried *in vacuo* at room temperature.

Table 2. Composition of the mixtures of homopolymers.

Name	pNIPAM (%)	pNEAM (%)
mNEAM ₂₅	75	25
mNEAM ₇₀	30	70
mNEAM ₉₀	10	90

The samples were designated mNEAM, where m means mixture, followed by the NEAM-content. For instance, a polymer whose content is around 90 % of NEAM, will be denominated as mNEAM₉₀. Then, polymer water solutions were prepared for analyzing the thermoresponsive behavior as a reference before preparing the new blends with CMC. The samples were placed inside a refrigerator (4°C) for homogenization.

Preparation of blends based on thermoresponsive polymers and CMC

The blends, composed of poly(*N*-isopropylacrylamide), poly(*N*-ethyl acrylamide), and CMC, were prepared in water and water/methanol at 0°C. A better homogenization of the samples was carried out through two steps. First, the polymers were dissolved in water and stored in the refrigerator for 24 hours, and subsequently, the CMC was added under stirring according to the proportions of Table 3. In the case of samples prepared in mixtures of methanol and water, the methanol was incorporated in the last step at low temperature (below LCST) using an ice bath. Finally, all the samples were stored in the refrigerator for 24 hours before analysis.

The blends were called using the name of the blends of homopolymers, followed by CMC whose molar mass is around 250000 g/mol and degree of substitution of the Na⁺ is 0.9. The MeOH was added to names for the blends performed in water/methanol mixtures. For instance, a blend composed of mNEAM₉₀ and CMC in water will be denominated as mNEAM₉₀CMC, while the same one in water/methanol will be identified as mNEAM₉₀CMC_{MeOH}. The list of the obtained samples is shown in Table 3.

Table 3. Composition of blends composed by polymers and CMC in water and water/methanol mixtures.

Name	Polymer concentration (wt. %)	CMC concentration (wt. %)	Water: MeOH (Ratio)
mNEAM ₂₅ CMC	10	2.5	100:0
mNEAM ₂₅ CMC _{MeOH}	10	2.5	50:50
mNEAM ₇₀ CMC	10	2.5	100:0
mNEAM ₇₀ CMC _{MeOH}	10	2.5	50:50
mNEAM ₉₀ CMC	10	2.5	100:0
mNEAM ₉₀ CMC _{MeOH}	10	2.5	50:50

Molecular characterization

The structure of the polymers was analyzed using nuclear magnetic resonance and gel permeation chromatography. The proton nuclear magnetic resonance spectra were performed in an AVANCE III 600 MHz spectrometer (Bruker, Karlsruhe, Germany) at 25 °C using deuterated D₂O. The molecular weights and distributions were studied using size exclusion chromatography (Waters e2695 Separation Module, Waters, Massachusetts, USA.) at 35 °C, using tetrahydrofuran as solvent (1 mL/min). The materials were also analyzed by Fourier transform infrared spectrometer (Nicolet 6700, Waltham, USA), samples were incorporated in tablets of potassium bromide.

Properties

The thermoresponsive behavior was analyzed using a UV-vis spectrophotometer (PerkinElmer UV/VIS Lambda 365) linked to a temperature controller (PerkinElmer 365K7010302, PerkinElmer, Massachusetts, U.S.A.). The samples (1 wt.%) were tested from 20 to 95 °C using a heating rate of 1 °C/min at 400 nm.

Dynamic Light Scattering (Zetasizer Nano ZSP, Malvern Panalytical, Malvern, United Kingdom) analysis was selected as another way for detecting the changes associated with the phase transition temperature. The experiments were carried out between 20 to 92 °C, using transparent cuvettes (quartz, Purshee, Beijing, China) for the blends (0.03 wt.%), and a heating rate of 2 °C/min.

The rheological measurements, using an Anton Paar MCR 302 rheometer (Graz, Austria), were performed to test for the LCST-behavior and the viscosity function. The analysis of LCST-behavior was obtained by temperature dependence measurements, which were evaluated using a heating rate $q = 1 \text{ K min}^{-1}$, angular frequency $\omega = 1 \text{ rad s}^{-1}$, and deformation amplitude $\gamma_0 = 1 \%$ (linear conditions) in humidity saturated atmosphere. A temperature range between 3 and 95 °C was tested. Dynamic frequency sweeps (DFS) tests were completed at angular frequencies ranging from 100 to 0.1 rad/s and using a shear deformation amplitude γ_0 of 1%. On the contrary, dynamic strain sweeps (DSS) had a fixed angular frequency of 1 rad/s and shear deformation amplitude between 0.01% to 1%. Both measurements were carried out at 3°C (below LCST), and the samples were isolated from the environment using a low viscous paraffin oil to avoid volatilization of the solvent.

Results and Discussion

The molecular characterization of obtained polymers was carried out through gel permeation chromatography and proton nuclear magnetic resonance. Figure 1a exhibits the GPC-data for mNEAM₉₀, where both peaks can be clearly detected for pNIPAM and pNEAM; the ratios of these two peaks belonging to the individual homopolymers.

The molecular weight and polydispersity indices (PDI - the ratio of weight M_w and number average molar mass M_n) of pNIPAM and pNEAM homopolymers were estimated from GPC-data, whose number average molar masses were $M_n = 29000 \text{ g/mol}$ (PDI=1.52) and 3500 g/mol (PDI=1.05), respectively, based on PS-standards. The differences between molecular weights could be associated with different effects associated with the chemical kinetics. The preparation of the different homopolymers, and the subsequent mixture, provided high homogeneity in the resulting structures. The homogeneity of the blends is assured because same homopolymers were used for their preparation.

The FTIR-spectra (Figure 1b) show similar structures for all the blends of homopolymers, as could be expected from the synthetic route, showing an excellent equivalence between samples.

The final structure of the pure polymers and blends was determined by a comparison between the spectra of proton nuclear magnetic resonance (Figure 1c), for which NMR-data can provide important information about the microstructure of the resulting polymers. Deuterated water (D₂O), used as a solvent, shows a clear peak located at 4.8 ppm [32]. The similarities between spectra indicate that structures are similar and can exclusively be attributed to differences in blend composition, as Figure 1c shows by the

isolated peaks associated with the methine of pNIPAM and the methylene of pNEAM placed at 3.9 ppm and 3.2 ppm, respectively [32].

The variation between properties must be predominantly linked to the ratio between homopolymers (Table 4). The relative composition between polymeric chains was also observed by ¹H-NMR, showing a good correspondence with the physical blends. It was estimated by the relationship between the methine of pure pNIPAM and the methylene of pNEAM for the different blends.

Table 4. Ratio between homopolymers for different blends.

Name	NIPAM [mol %]	NEAM [mol %]
mNEAM ₉₀	8	92
mNEAM ₇₀	21	69
mNEAM ₂₅	75	25

The phase transition temperature associated with the LCST was studied for all the original mixtures of homopolymers. This study could explain the effects of the molecular features on the final LCST through the sensibility obtained by rheology. In this context, the verification of the rheological data was carried out using UV-vis spectroscopy and dynamic light scattering, where other important information can also be achieved.

Figure 2a exhibits the data derived from UV-vis spectroscopy, where two phase transition temperatures can be detected for polymeric water solutions of mixtures of homopolymers (1 wt.%). The transition placed at a lower temperature can be identified as the LCST of pNIPAM, due to the LCST related to PNIPAM is defined around 32 °C [33,34]. On the other hand, the second LCST placed at higher temperatures is associated with pNEAM, whose values were previously found to be between 62 and 82 °C depending on the measurement method and molar mass [35-37]. Clearly, both LCSTs can be identified for all mixtures with the transmission between the LCSTs scaling with the mixing proportion. However, the curve of mNEAM₇₀ is very close to mNEAM₂₅, suggesting a nonlinear dependence, which is due to the nature of the transmission reduction. It could be understood by considering this to be the consequence of a threshold-type behavior, i.e. the reduction of transmission follows a sigmoidal function with the switching concentration being between 90 and 70% pNIPAM. Furthermore, mNEAM₉₀ shows an increase in transmittance above 40°C before decreasing again due to the LCST of pNEAM, which could be understood as the consequence of the pNIPAM chains clustering into bigger, less light scattering clusters that could also move out of the observation range as they might sink downwards in the vial owing to a higher density.

The thermoresponsive behavior was also studied by dynamic light scattering (Figure 2b) using a polymeric concentration in water of 0.03 wt.%. Again, both transitions are identified through the ratio between polymeric chains associated with pNIPAM and pNEAM. Furthermore, the trend and temperatures followed the behavior described by UV-vis spectroscopy [38,39]. The LCST of pNIPAM leads to an increase of the Z-average particle size ($Z_{AVERAGE}$), where mNEAM₉₀ and mNEAM₇₀ show almost identical values between 35 and 75°C (above the LCST of pNIPAM but below the LCST of pNEAM), suggesting that the pNIPAM colloidal particles are sufficiently small to remain non-percolated. Upon reaching the LCST of pNEAM at 75-80°C, the high fraction of pNEAM in mNEAM₉₀ and mNEAM₇₀ lead to a rapid increase of Z-average particle size owing to percolation of the formation of a hydrophobic polymer chain network. mNEAM₂₅ in contrast shows much higher Z-average particle size above the LCST of pNIPAM and only a moderate further increase at the LCST of pNEAM, which is the consequence of the much higher pNIPAM content. The results overall suggest that the hydrophobic clusters formed by pNIPAM are denser and therefore also smaller than those formed by pNEAM, making them appear bigger in light scattering.

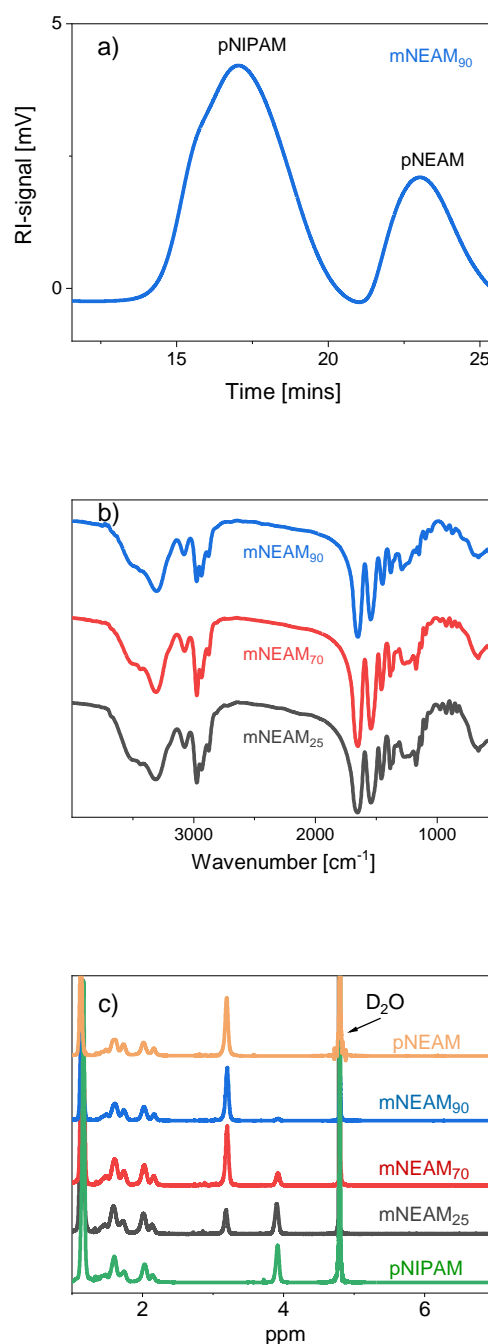


Figure 1. Molecular characterization of polymers and blends obtained by GPC (a), FTIR-spectra (b), and ¹H-NMR (c).

Figure 2c shows the rheological analysis for all the blends, where the transitions being evident as an increase of the magnitude of complex viscosity $|\eta^*|(T)$ confirm the previous results of UV-vis spectroscopy and dynamic light scattering. These results can be directly associated with the microstructure of the polymers studied [33,40,34]. Only two transitions are detected, as it could be expected from the preparation route, i.e., as the mixtures are not copolymers, there are no other effects associated with random sections composed by NIPAM and NEAM [33,40,34]. On the other hand, the abrupt fall exhibited by mNEAM₂₅ after the first phase transition temperature can be explained through artifacts, which were discussed in detail elsewhere [41]. It is well established that the LCST of pNIPAM is rather pronounced [41] 75% of mNEAM₂₅ are in pNIPAM-chains, which, therefore, will dominate the rheological behavior.

Valuable information can be achieved by comparing LCSTs estimated by UV-vis spectroscopy, dynamic light scattering, and rheology of both constituents (Figure 2d).

The cloud temperatures (CP) were calculated at 50 % of the transmittance value change, the phase transition temperature (PT) from dynamic light scattering was estimated at 50 % of the collapse transition, and the transition temperature (LCST_R) derived from rheology was elected as the half-height of the increase in $|\eta^*|$. Figure 2d exhibits all the LCSTs calculated by these methods as a function of the ratio between pNIPAM and pNEAM. The highest phase transition temperatures show a clear trend for all the techniques, i.e., the phase transition temperature decreases when pNEAM-ratio rises.

The overall trend is that increasing the pNEAM-content (and decreasing the pNIPAM content) leads to a decrease of the LCST of pNIPAM and pNEAM by 3.4 K and 9.8 K, respectively. It is well established that the LCST of pNEAM varies in a much larger range than its pNIPAM-counterpart, although mostly that was attributed to the molar mass only [33]. In general, increasing the pNEAM content should increase the LCST in random copolymers as was explained before [17], but these systems are composed of simple mixtures of pNIPAM and pNEAM homopolymers. Thus, the collapse of the pNIPAM chains could partially restrict the hydrophobic interactions between other polymeric chains. If more pNIPAM chains are collapsed, a lower number of pNEAM chains could interact between them and other polymeric chains, and therefore the LCST would be higher. Nevertheless, if more pNEAM-chains interact between them and surrounding polymeric chains, the LCST will decrease due to a lower content of pNIPAM-chains contracted.

The polymer concentration does not show a clear trend as measurements are carried out through different techniques, as it can be deduced from the phase transition temperatures of rheology (10 wt.%), light scattering (0.03 wt.%), and UV-spectroscopy (1 wt.%). Nevertheless, the error derived from measurements should be considered, and other parameters could also be involved. This finding does not invalidate the idea of a small concentration dependence; e.g. determining the LCST by DSC, as the effect of concentration is small but systematic [40,33].

Possible reasons for the concentration dependence of the LCST of pNEAM could be the presence of globules of insoluble pNIPAM chains that due to their small size at low pNIPAM-contents could lead to an LCST at lower temperature than at higher pNIPAM-contents, which should have larger insoluble clusters. The dependence of the LCST of pNIPAM on its content could be due to Hofmeister arguments [42], making pNEAM behave chaotropic. One might argue the same for the role of pNIPAM for the pNEAM-LCST, but unlike in the former case, pNIPAM is hydrophobic and phase-separated, so it cannot behave like a dissolved component. These phenomena could also understood in terms of loss of order in the water molecule arrangement around the hydrophobic chains and intramolecular hydrophobic interactions between isopropyl and ethyl groups that are dominating at lower pNIPAM concentrations or less hydrogen bonding moieties that are responsible for lowering LCST [43]. At higher concentrations of pNIPAM the mobility and the availability of hydrogen bonding moieties are higher and ultimately the entropic mixing effect is also smaller because of larger size particles, hence does not allow better intermolecular hydrophobic interactions, which results in higher LCST [44].

The blends composed of polymers and CMC were prepared in water and mixtures of water and methanol, as explained in the Experimental Part. The blends, performed in water, are transparent and show a slightly higher density than normal polymeric solutions. Appreciable changes between the constituent contents cannot be observed with the naked eye. Nevertheless, the situation changes when the samples are prepared in mixtures of methanol and water. In that case, sample density suddenly increases, and the systems become opaque and whitish due to cononsolvency, which varies depending on the ratio between homopolymers. Furthermore, these changes can be also explained through previous works where authors described an increase of viscosity in Na-CMC solutions prepared in mixtures of ethylene glycol/water and methanol/water, which is related to the physical cross-linking of CMC [1,8].

In addition, the white color could be explained by the cononsolvency phenomenon, where a mixture of solvents behaves as poor solvent at specific ratios but separately are good solvents for the same polymer [17,21-23]. The gelation produced by the physical cross-linking of CMC seems disrupted by the presence of the polymers, and probably by the cononsolvency phenomenon.

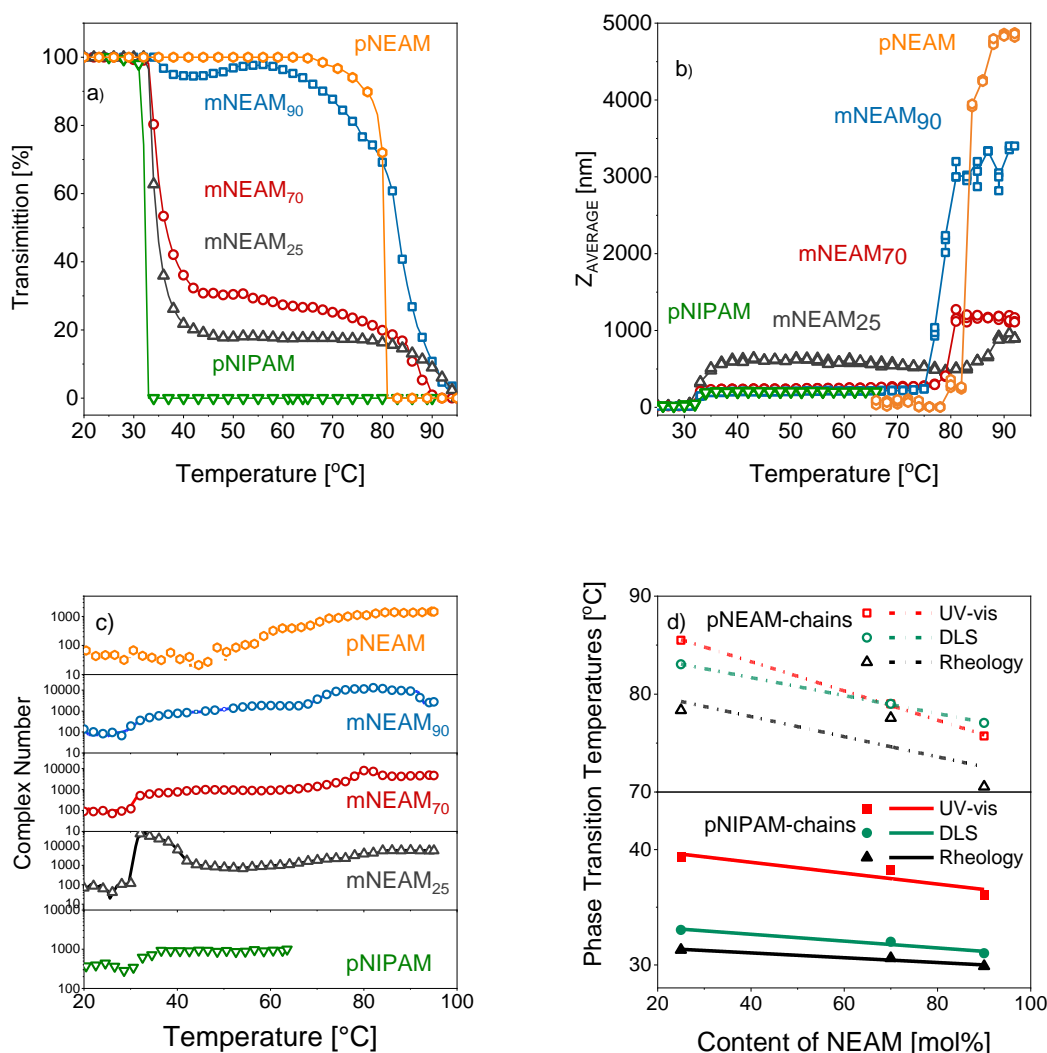


Figure 2. Phase transition temperatures analyzed for all the blends composed by pure polymers by UV-vis spectroscopy [1wt.%] (a), dynamic light scattering [0.03wt.%] (b), and rheology [10wt.%] (c). LCSTs of pNEAM and pNIPAM vs. pNEAM-content (d).

The high density and turbidity of the obtained blends in methanol/water reduce the number of techniques able to detect the changes in the phase transition temperature to non-optical techniques. Rheology can get an insight into these samples, as the sample transparency does not influence the mechanical properties, although in many cases, they are related through various processes influencing both properties simultaneously.

The blends prepared in water (Figure 3) clearly show both transitions also observed in the polymeric water solutions, but both phase transition temperatures decrease due to the presence of CMC. Higher contents of ions induces a lower phase transition temperature [11]. Furthermore, the LCST is very similar independently of the ratio of pNIPAM and pNEAM, which is a clear indicator of the independence between of different polymeric chains, as for a random-copolymer, the LCST-temperatures would vary systematically with comonomer content [45,37,17,46].

The presence of CMC decreases the LCST as it could be expected by the introduction of ions inside the polymeric solution in accordance with Hofmeister series argu-

ments[42]. Thermo-thickening behavior is not observed, i.e., the viscosity does not rise when the temperature increases [47].

The samples performed in methanol and water (Figure 3) exhibit an unusual behavior, as the first LCST (associated with pNIPAM-chains) cannot be observed. The co-solvency could explain this effect because pNIPAM shows no or only a weak LCST in mixtures of methanol and water (1:1) once the methanol content exceeds ca. 30% [45,17,48,37,46]. This fact could be attributed to the hydrophobic behavior of the pNIPAM polymeric chains. Nevertheless, the LCST of pNEAM can be clearly detected, as hydrophobic polymers display a better co-solvency than hydrophilic polymers [17]. In addition, the phase transition temperature is ca. 4-5 K lower than in aqueous solutions in the presence of MeOH [17].

The phase transition temperatures of the blends were estimated as explained before. Figure 4a exhibits the phase transition temperatures of pNIPAM-chains, where the blends show a small decrease in the LCST-values due to the presence of ions [41]. Like for the samples without CMC, a slight decrease in phase transition temperature can be detected when the content of pNEAM-chains increases. As the samples are composed of the same homopolymers at different mixing ratios, a molar mass or structure (e.g. tacticity) influence can be discarded. In this sense, the molar mass could play an important role as molar mass of pNEAM ($M_n = 3500$ g/mol) is rather lower than pNIPAM ($M_n = 29000$ g/mol), i.e., if the pNEAM amount increases consequently the interactions between polymeric chains raise. This behavior is also exposed by the highest phase transition temperatures of pNEAM-chains in Figure 4b, where clearly, the amount of interactions associated with pNEAM decreases the LCST for mNEAM_x.

The collapse of the pNIPAM-chains after the first phase transition temperature associated with LCST could be involved in the trend of LCST described by mNEAM_x samples when pNEAM content rises. The collapse of the pNIPAM-chains could decrease the interactions between polymeric chains of pNEAM, specifically when more pNIPAM chains are inside of the solution. Nevertheless, if the content of pNEAM increases regarding to pNIPAM, the highest LCST could decrease as interactions between chains rise. In this case, that effect could justify the change between mNEAM₂₅ and mNEAM₉₀, where the collapse of the pNIPAM-chains shows a variation of 7 K between both samples.

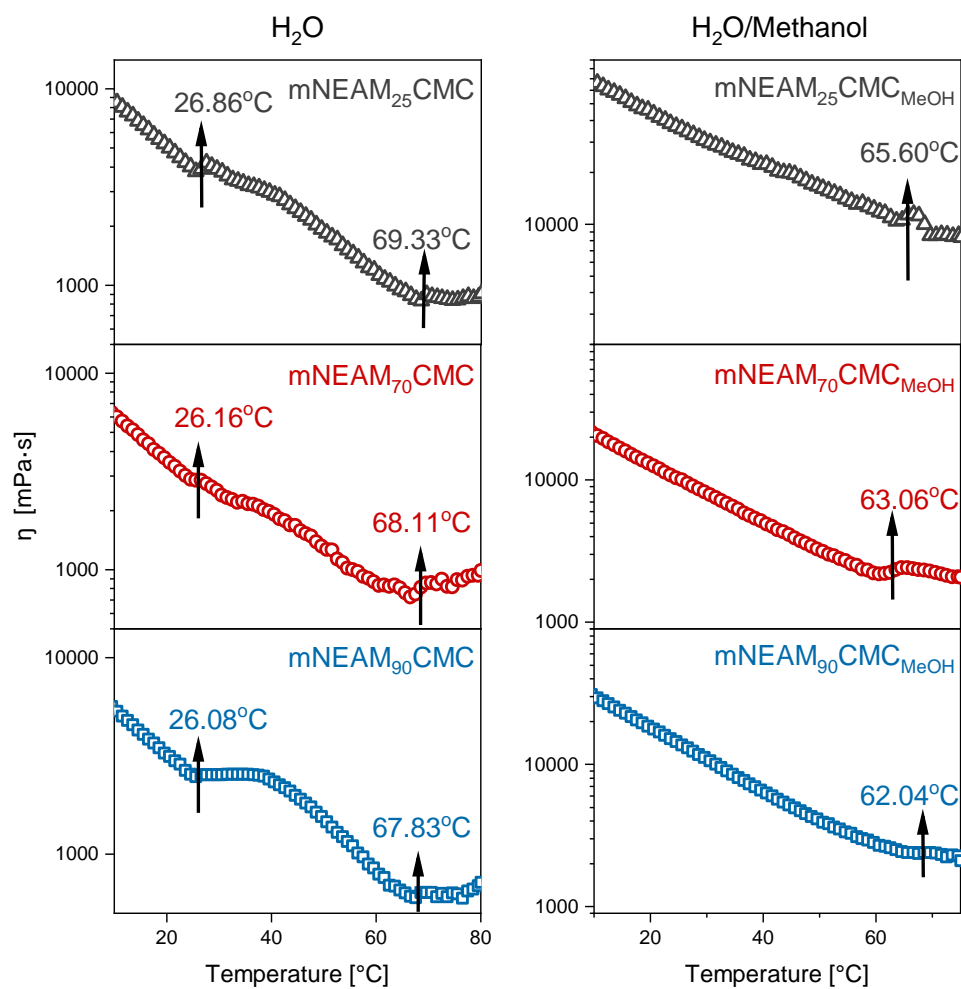


Figure 3. Complex viscosities as a function of the temperature of blends prepared in water (a) and water/methanol (b).

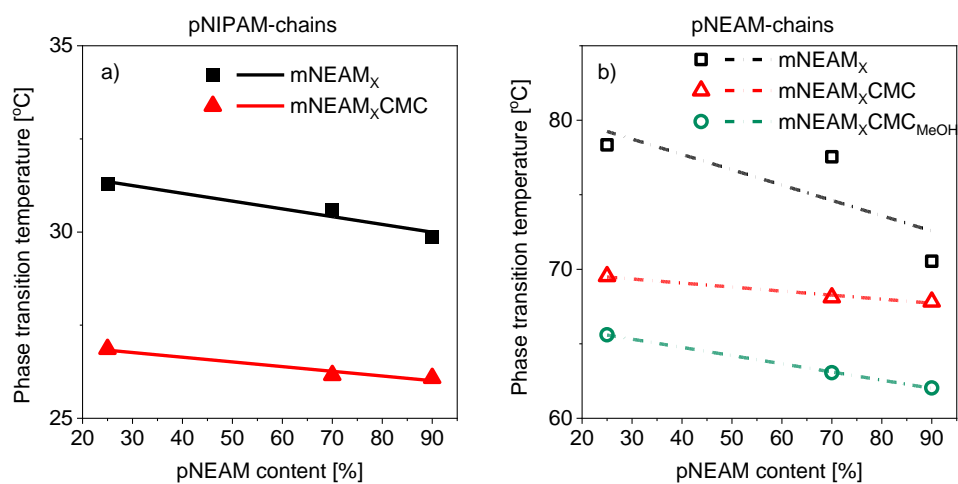


Figure 4. Phase transitions temperatures of polymers and blends associated with pNIPAM-chains (a) pNEAM-chains (b).

The presence of CMC reduces the LCST due presence of ions. This fact is also supported by a lower slope of the mNEAM_xCMC samples compared to mNEAM_x mixtures.

The decrease of the phase transition temperature associated with LCST due to the presence of CMC shows a minimum for mNEAM₂₅CMC which value is lower than 10 K regarding to mNEAM₂₅. Similar transition temperatures are observed for mNEAM₇₀CMC and mNEAM₉₀CMC, exhibiting the strong effect of ions over LCST regarding other parameters as the ration between both homopolymers.

The subsequent addition of methanol decreases the LCST in similar way than the addition of CMC, because a higher content of ions is inside the solution. The lack of sensitivity associated with the LCST of pNIPAM, probably promoted by the cononsolvency effect, together with the effect of the hydrogen bonds of the physical crosslinking between CMC and methanol would affect the LCST-behavior and consequently a deep study should be carried out.

The gelation was studied through linear viscoelasticity analysis using small amplitude oscillatory shear (SAOS) for all the blends performed in water (a) and water/methanol (b) at 3 °C (Figure 5).

The aqueous samples show the typical behavior of a polymer solution or melt in the terminal regime. One might argue that mNEAM₂₅CMC and mNEAM₇₀CMC show a small upturn of the storage modulus towards low angular frequency ω , suggesting some kind of slow relaxation process being present. This slow relaxation process could be related to the bridging of CMC molecules by pNIPAM, as it disappears at the lowest pNIPAM-contents which could be explained through the physical crosslinking of CMC. In all other aspects, the data look very similar to each other, being typical for the terminal regime of a polymer solution. This is logical considering that only the blend ratio of pNIPAM and pNEAM was changed. The CMC was the same for all the experiments, and exclusively, changes in gelation can be associated with the polydispersity and ratio between pNIPAM and pNEAM homopolymers. Then, the differences could be associated with the interactions between pNIPAM, pNEAM and CMC where a competition between different hydrogen bonding is happening [1]. When disregarding the difference in thermoresponsive behavior, which can be neglected here, as 3°C is significantly below the LCST, the somewhat higher moduli of mNEAM₂₅CMC are the consequence of this material's higher molar mass, shifting the terminal relaxation and thus increasing the moduli.

Upon adding methanol, the moduli increase significantly and the behavior of the materials bears some similarity with that of a critical gel, i.e., a more or less frequency-independent phase angle δ of $\approx 45^\circ$ [49]. The formation of any gel is accompanied by either jamming or some kind of network formation which could be associated with the physical crosslinking between the CMC and methanol. In this case, water-methanol mixtures lead to a dramatically reduced solubility of the homopolymers in the blends as discussed before owing to cononsolvency. When looking at the data in more detail, it becomes obvious that the higher the pNEAM-content, the less the rheological data differs from the behavior of a polymer solution (see e.g. Fig. 5a). Higher pNEAM-contents lead to the presence of a slow process, which is obvious a reduction of G' -slope at low frequencies. Considering the cononsolvency, this process is most likely caused by some insoluble fractions of the homopolymers, in particular the pNEAM, in which more or less hairy colloidal particles interact with each other. In comparison to the unentangled polymer solution, such interactions lead to an increase in viscosity overall.

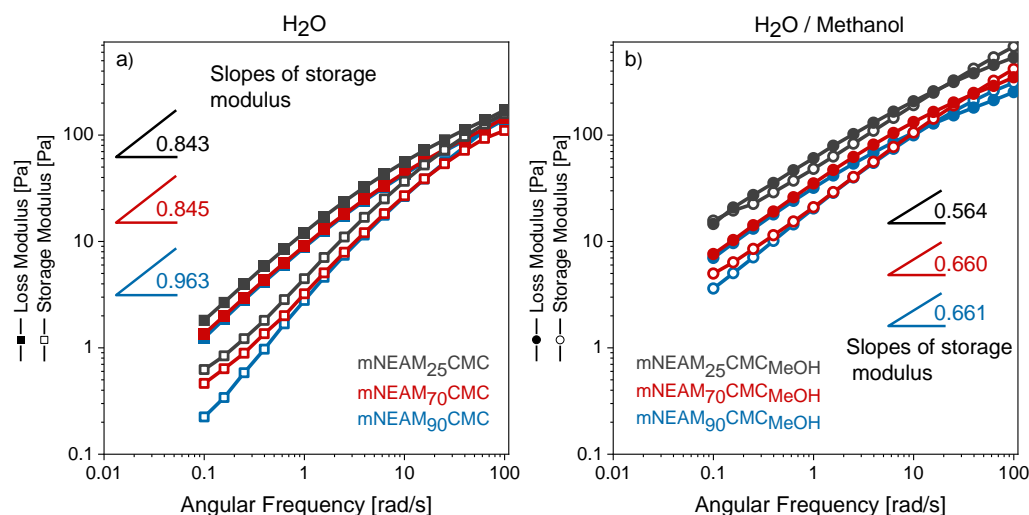


Figure 5. Mechanical spectra for blends prepared in water (a) and water/methanol (b).

The gelation of CMC through physical cross-linking seems evident in Figure 5b regarding Figure 5a. All the trends are similar but slightly lower than samples prepared in water due to the hydrogen bonds associated with CMC in mixtures of propylene glycol and water[1]. On the other hand, the cononsolvency phenomenon is also presented in the pNIPAM-chains, such as it can be deduced through the milky samples obtained and the absence of LCST-signal in mixtures of water/methanol (right side of Figure 3). Interaction between hydrogen bonds associated with pNEAM-chains could be minimized due to the cononsolvency behavior that could affect to the pNEAM too, and the LCST related to pNEAM-chains which occurs at really high temperatures.

Thus, the partial gelation due to hydrogen bonds of CMC seems slightly affected by the LCST-phenomenon of the blends of homopolymers, i.e., the cononsolvency effect observed in solutions prepared in water/methanol mixtures could restrict the hydrogen bonds of the physical crosslinking depending on the ratio between pNIPAM and pNEAM. On the other hand, the pNIPAM could induce the formation of clusters which isolate the thermoresponsive blend of homopolymers regarding the CMC.

Figure 6 shows the responses of the complex viscosity $|\eta^*|$ as a function of shear strain γ_0 for the different blends prepared in water and water/methanol mixtures. The samples performed in water show lower complex viscosities than other blends performed in water/methanol mixtures, which agrees with the frequency dependence (Fig. 5). The nonlinearity limit, defined by the deformation γ_0 , at which the material functions (here $|\eta^*|(\gamma_0)$) shows a 5% change from the linear viscoelastic behavior ($\gamma_0 \rightarrow 0$). For polymer solutions and melts, as well as for colloidal polymer gels, whose colloidal nature is not too dominating, the nonlinearity limit is usually around $\gamma_0=30\%$ [50-53]. For any system with clear phase boundaries, however, the nonlinearity limit is reduced significantly. Typical colloidal systems have a linearity limit γ_0 around 1%, but it can also be significantly lower [50]. The nonlinearity limits for the aqueous system is ca. 60%, suggesting that they behave like classical solutions, while for the methanol-water systems, nonlinearity limits around 6% were found, which indicates that the system has some clearly colloidal behaviors, which agrees to the cononsolvency discussion before, as a partial phase separation is introduced.

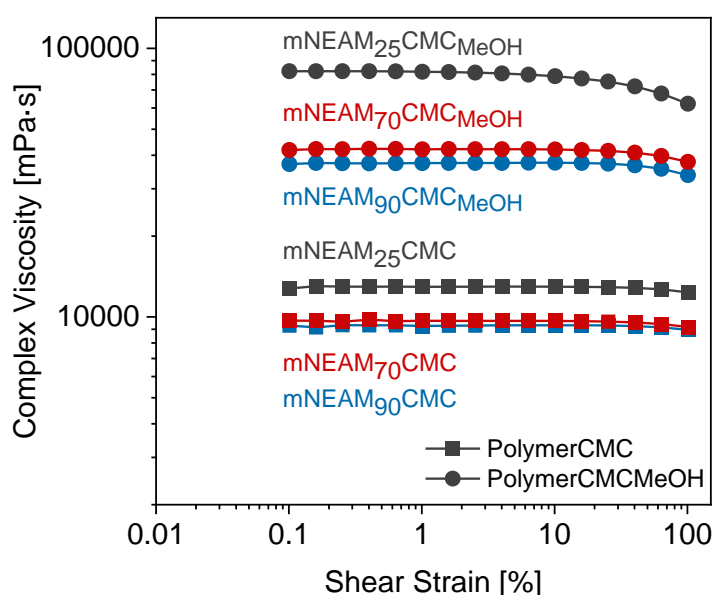


Figure 6. Complex viscosity as a function of shear strain (DSS) for the different blends at 3 °C.

Conclusions

New blends consisting of homopolymers (pNIPAM and pNEAM), and CMC were formed in water and 1:1 water/methanol mixtures. The molecular features were studied, and results were used for explaining the thermoresponsive behavior measured by rheology.

The introduction of CMC lead to a decrease in the LCST, while increasing the pNEAM/pNIPAM ratio moderately decreased the LCST. No thermothickening behavior, typical for CMC, is observed for the blends, probably affected by the presence of pNEAM-chains, which could disrupt the hydrogen bonds performed between CMC and –OH groups.

The samples performed in mixtures of methanol and water exclusively exhibit the pNEAM-LCST, while the pNIPAM-LCST is undetectable due to cononsolvency.

Finally, it was observed that hydrophilic pNEAM-chains could disrupt the hydrogen bonds between the CMC and methanol, negatively affecting the gelation. This fact explains that the hydrogen bonds of LCST and physical cross-linking could compete, opening a new perspective in this research field.

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Declarations

Conflicts of interest

The authors declare that they have no conflicts of interest.

Statements on compliance with ethical standards and standards of research involving humans and animals

This article does not contain any studies involving animals performed by any of the authors. This article does not contain any studies involving human participants performed by any of the authors.

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