# Solubility and Thermoresponsiveness of PMMA in Alcohol-Water Solvent Mixtures

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To reduce the environmental burden of polymer processing, the use of non-toxic solvents is desirable. In this regard, the improved solubility of poly(methyl methacrylate) (PMMA) in ethanol/water solvent mixtures is very appealing. In this contribution, detailed investigations on the solubility of PMMA in alcohol/water solvent mixtures are reported based on turbidimetry measurements. PMMA revealed upper critical solution temperature transitions in pure ethanol and ethanol/water mixtures. However, around 80 wt-% ethanol content a solubility maximum was observed for PMMA as indicated by a decrease in the transition temperature. Moreover, the transition temperatures increased with increasing PMMA molar mass as well as increasing polymer concentration. Careful analysis of both heating and cooling turbidity curves revealed a peculiar hysteresis behaviour with a higher precipitation temperature compared with dissolution with less than 60 wt-% or more than 90 wt-% ethanol in water and a reverse hysteresis behaviour at intermediate ethanol fractions. Finally, the transfer of poly(styrene)-*block*-poly(methyl methacrylate) block copolymer micelles from the optimal solvent, i.e. aqueous 80 wt-% ethanol, to almost pure water and ethanol is demonstrated.

## Introduction

The solubility of polymeric materials is of major importance for a wide range of applications including personal care, e.g. creams and other liquid formulations, and biomedical, e.g. drug delivery. In addition, such applications require biocompatible polymers and low-toxicity solvents, like water and ethanol, thus severely limiting the number of applicable polymers to polar hydrophilic structures. However, Shultz and Flory[1] as well as Wolf and Blaum[2] have demonstrated that the solubility of polymers can be affected in an unpredictable way using binary solvent mixtures resulting, in some cases, in improved solubility compared with the individual solvents.

Only little is known about polymer solutions in water/ethanol mixtures despite the fact that these solvent mixtures exhibit interesting abnormal properties due to the presence of hydration shells around the ethanol molecules.[3–5] For instance, the presence of such hydration shells has been reported to result in solubility maxima for drug molecules in water/ethanol mixtures.[6–8] In addition, solubility maxima have been reported for thermoresponsive polymeric gels based on 2-hydroxyethyl methacrylate and acetoacetoxyethyl methacrylate exhibiting upper critical solution temperature (UCST) behaviour, i.e. the polymer is insoluble at low temperatures and dissolves upon heating the solution.[9] The solubility maximum in ethanol/water solvent mixtures was observed around 40–50 mol-% ethanol and was ascribed to the formation of water-cages around the more hydrophobic ethanol molecules. A similar explanation was provided for the unexpected presence of an UCST for poly(*N*-isopropyl acrylamide) in ethanol/water mixtures with 0.28 to 0.35 mol-% ethanol, whereby it was noted that at elevated temperatures the water-cages are most likely broken liberating the ethanol molecules that enhance the solubility of the polymer.[10]

In addition, it is known that poly(methyl methacrylate) (PMMA) dissolves in ethanol/water solvent mixtures while being insoluble in both water and ethanol at ambient temperature;[11–13] although a UCST of ~87°C was reported for PMMA in pure methanol as well as in ethanol.[14] In contrast to the previously discussed polymers, the solubility maximum for PMMA in ethanol/water mixtures was reported at 80 vol-% ethanol indicating that preferential water-hydrogen bonding to
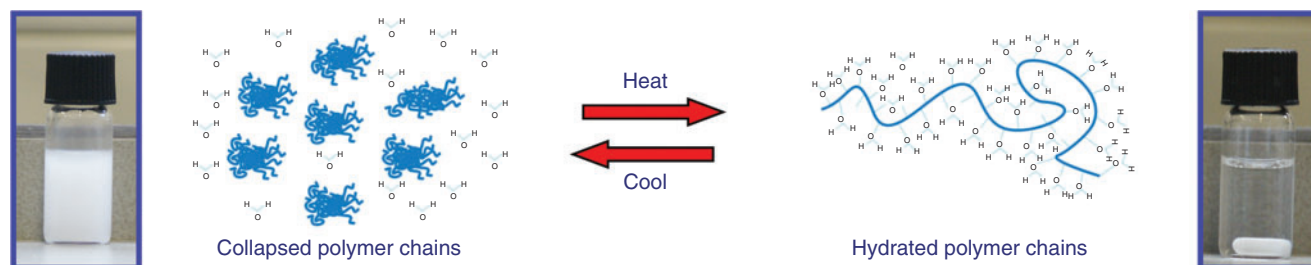
**Fig. 1.** Schematic representation of the upper critical solution temperature transition of a polymer solution.

the ester moieties of the polymer are responsible for the cosolvency instead of the water-cage around the alcohol.[11,15] The hydration-shell that is formed around the carbonyl groups of the polymer can act as a compatibilizing layer between the polymer and ethanol. Recently, we confirmed this hypothesis by small angle neutron scattering, indicating the presence of a single deuterated water molecule per PMMA repeat unit.[16] Polymer hydration is most pronounced in 80 vol-% ethanol since in this solvent mixture mostly single, non-clustered water molecules are present that effectively hydrogen bond to the polymer without breaking the stronger water-water hydrogen bonds.[5] Further increasing the amount of water increases the polarity of the solvent mixture and leads to the formation of water clusters, which decreases the polymer solubility by the necessity of breaking water-water hydrogen bonds for the formation of a hydration shell. Similar solubility results in ethanol/water mixtures were reported for poly(2-phenyl-2-oxazoline) (PPhOx) and copolymers thereof.[17,18] The structures of PPhOx and PMMA seem to be rather similar; in both cases the polymers contain hydrophobic side chains (phenyl or methyl) and hydrogen bond accepting groups (amide or ester) close to the polymer backbone. Besides the improved solubility, PMMA also exhibits an UCST in ethanol/water mixtures,[14] which we recently applied to develop thermoresponsive poly(styrene)-*block*-poly(methyl methacrylate) (PS-PMMA) micellar gels.[15]

In the current work, we further investigated the UCST behaviour of PMMA in alcohol/water solvent mixtures, whereby the cloud points and hysteresis between heating and cooling were determined as function of the molar mass and concentration of PMMA, the alcohol fraction in the aqueous solution as well as the nature of the alcohol, namely methanol, ethanol, or isopropanol. Furthermore, preliminary results are reported for the transfer of PS-PMMA micelles from 80 wt-% ethanol solutions into pure water or ethanol resulting in stable dispersed nanoparticles.

## Experimental

### Materials

Absolute ethanol was obtained from Biosolve Ltd and used within 1 month after opening of the bottle to prevent significant water attraction. Demineralized water was used in all experiments. The PMMA homopolymers (PMMA-14K: $M_n =$ 13.8 kDa, PDI = 1.18; PMMA-28K: $M_n = 27.4$ kDa, PDI = 1.43) were prepared by ATRP as described previously.[19] The PS-PMMA block copolymer ($M_{n,SEC} = 13.9$ kDa; PDI$_{SEC} =$ 1.16; DP$_{styrene} = 88$ (from SEC); and DP$_{MMA} = 80$) synthesis was also reported elsewhere.[20]

### Instrumentation

The turbidity measurements were performed in a Crystal16 turbidimeter from Avantium Technologies. The transmittance was

measured during two controlled heating/cooling cycles from −15°C to 75°C with a heating rate of 1.0°C per minute. The second cycle was used to determine the transition temperatures at 50% transmittance.

Transmission electron microscopy (TEM) measurements were performed on a FEI Tecnai 20, type Sphera TEM operating at 200 kV (Laboratory$_6$ filament). Images were recorded with a bottom mounted 1 k × 1 k Gatan CCD camera. TEM grids, 200 mesh carbon coated copper grids, were purchased from SPI. Prior to blotting, the grids were made hydrophilic by surface plasma treatment using a Cressington 208 carbon coater operating at 5 mA for 40 s. For sample preparation, 15 μL aliquots were applied to a 200 mesh carbon coated copper grid and subsequently the excess of liquid was quickly blotted away with filter paper.

### Micellization Procedure

The PS-*b*-PMMA block copolymer (2.0 mg) was weighed into a HPLC vial covered with a screw cap containing a hole and a septum and 1.0 mL ethanol/water (80/20 wt-%) solvent mixture was added. Subsequently, this mixture of solid polymer and solvent was heated with a heat gun until a slight overpressure was noticed by expansion of the septum. The micellar solution was obtained by cooling to ambient temperature.

The other micellar solutions were obtained by adding 100 μL of this initial micellar solution into ethanol or water resulting in transparent micellar solutions in 98 and 8 wt-% aqueous ethanol solutions, respectively.

**Caution:** Always use high quality HPLC vials covered with a screw cap with a hole and a septum, which acts as pressure valve, upon heating beyond the boiling point of the solvents for the preparation of the micelles to prevent too high overpressures potentially leading to explosion of the vial.

## Results and Discussion

The UCST of a polymer represents the lowest temperature in the phase diagram of the polymer-solvent mixture where the system undergoes a phase transition from two phases, namely a polymer rich and a solvent rich phase, to one homogeneous solution phase as schematically depicted in Fig. 1. This polymer solution phase transition is accompanied by a visual transition from a cloudy solution below the transition temperature to a clear solution above this temperature.

In the current work, the UCST phase transition is estimated by determination of the clearance point (CP$_h$) upon heating as well as the cloud point upon cooling (CP$_c$) at a fixed polymer concentration using turbidimetry. To avoid artefacts due to the history of the polymer samples, the second heating and cooling runs are evaluated to determine the CP$_h$ and CP$_c$, respectively, at 50% transmittance. Typical transmittance versus temperature
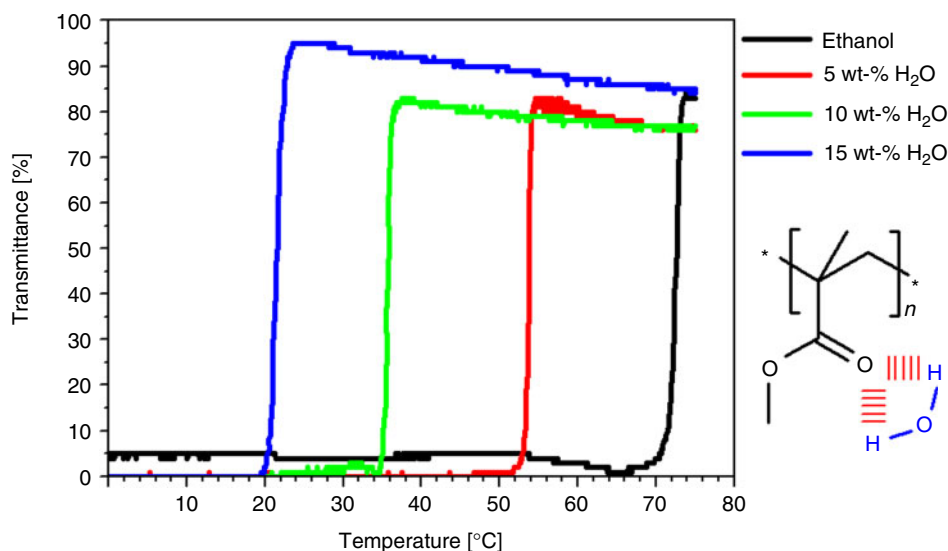
**Fig. 2.** Transmittance versus temperature plots for 0.5 wt-% PMMA-28k solutions in different ethanol/water solvent mixtures obtained during the second cooling run, showing precipitation of the polymer from solution. A schematic representation of the structure of the hydrated PMMA is also shown at the bottom right.
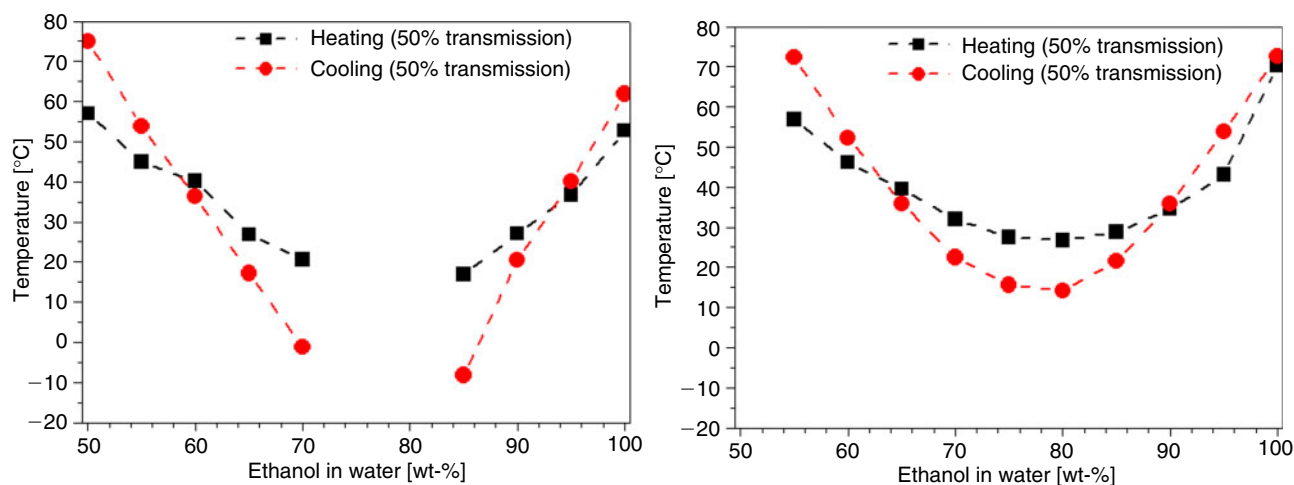


**Fig. 3.** Clearance points upon heating and cloud points upon cooling as a function of ethanol content in 0.5 wt-% aqueous solutions of PMMA-14k (left) and PMMA-28k (right).

plots are shown in Fig. 2 for PMMA-28k during the second cooling run revealing a sharp transition from high transmittance to 0% transmittance indicative of the precipitation of the polymer. The slight variation in the high transmittance value is due to the baseline correction of the sensors in the turbidimeter as well as a slight temperature-sensitivity of this sensor. The slight increase in transmittance of the sample in pure ethanol upon further cooling is due to sticking of the polymer to the vial walls as confirmed by visual inspection. Nonetheless, the most important observation of these turbidity curves is the significant decrease in $CP_c$ upon addition of small amounts of water to the ethanol solution indicating the co-solvency effect for PMMA due to hydration of the ester groups resulting in a kind of 'compatibilizing' hydration layer in between the polymer and the solution, as shown in Fig. 2, bottom right.[15]

The $CP_c$ and $CP_h$ values obtained by turbidimetry as a function of ethanol content in the aqueous ethanol solutions are

plotted in Fig. 3 for PMMA-14k and PMMA-28k (0.5 wt-%). Both polymers show similar trends although PMMA-28k is slightly less soluble as indicated by the higher transition temperatures. In fact, PMMA-14k does not phase separate upon cooling down to −15°C with 70 to 85 wt-% ethanol while PMMA-28k does. When looking in more detail to the transition temperatures of PMMA-14k, it is striking that the hysteresis between heating and cooling reverses depending on the ethanol content. For the good solvent mixtures, i.e. for the lower transition temperatures dissolution upon heating occurs at a higher temperature compared with precipitation upon cooling indicating that the hydrated polymer chains are energetically more favourable compared with the two-phase system of precipitated polymer globules and an ethanol/water solvent phase. This lower $CP_c$ compared with $CP_h$ can be ascribed to the presence of mostly single, non-clustered water molecules in this ethanol concentration regime (i.e. the absence of a strong hydrogen bonded water
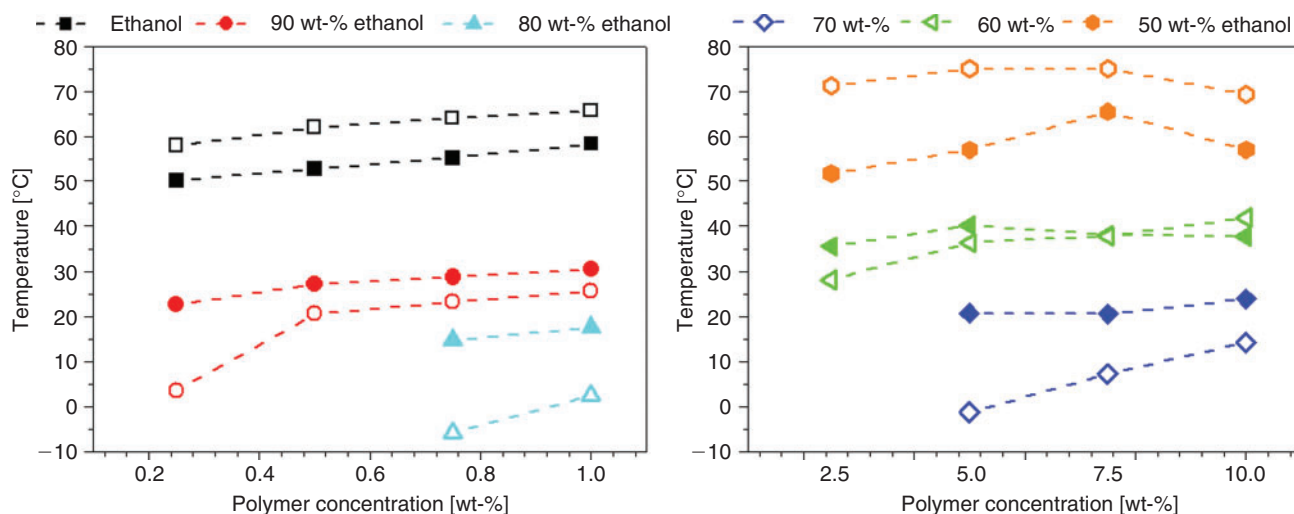
**Fig. 4.** Clearance points upon heating (closed symbols) and cloud points upon cooling (open symbols) as function of PMMA-14k polymer concentration at different ethanol contents (see legend).

network)[5] resulting in more favourable hydrogen bonding of water to the PMMA ester groups since these are stronger compared with the hydrogen bonds of single, non-clustered water molecules with ethanol in solution. In addition, the dissolution of the precipitated polymer globules occurs at a higher temperature compared with precipitation, which is most likely due to the loss of entropy caused by stretching of the polymer chains. This is required for the full hydration of all ester groups, as was found to be the case in solution,[16] upon dissolution. For PMMA-28k, the decrease in entropy upon dissolution is larger resulting in a strong increase in $CP_c$ compared with PMMA-14k while $CP_h$ is only slightly increased. In contrast, in pure ethanol and ethanol containing a minor water fraction, the polymer phase transition is driven by the change in solvent polarity upon heating and the hydration of the polymer is less important. As such, the entropy loss upon unfolding of the polymer chains is not over-compensated by strong specific hydration of the ester groups resulting in a slightly higher $CP_c$ compared with $CP_h$. At an ethanol fraction lower than 60 wt-%, the $CP_c$ is also higher than the $CP_h$, which can be ascribed to the presence of larger water clusters in solution. As such, the hydrogen bonding of water is stronger in solution compared with the hydration of the ester groups explaining the observed hysteresis. It should be noted that the heating and cooling rate during the turbidimetry measurements might also influence the observed hysteresis. In addition, turbidimetry is limited to the detection of large globules that scatter the transmitted light, which results in oversimplification of the phase transition events by exclusion of the formation of smaller polymer globules as well as strongly solvated transparent globules.

The influence of the polymer concentration on the phase transitions was evaluated for PMMA-14k in a limited range from 0.25 to 1.0 wt-% in various ethanol/water solvent mixtures (Fig. 4). In general, the transition temperatures increase with increasing polymer concentration, which can be ascribed to an increase in polymer-polymer interactions in solution commonly observed in the low polymer concentration regime.[21–23] A similar reversal of $CP_c$ and $CP_h$ is observed with variation of the ethanol fraction as discussed above for 0.5 wt-% PMMA concentration, independently of the polymer concentration. It should be noted that for most solvent mixtures the extent

of hysteresis decreases with increasing polymer concentration, which might be ascribed to the formation of smaller aggregates at lower polymer concentration resulting in decreased scattering as has been reported for lower critical solution temperature polymer transitions.[24,25] Surprisingly, the hysteresis reverses with increasing polymer concentration for the aqueous polymer solution with 60 wt-% ethanol. At up to 0.5 wt-% polymer concentration, $CP_h$ is higher than $CP_c$, at 0.75 wt-% both transitions occur at equal temperatures while at 1 wt-% polymer concentration, $CP_c$ is higher than $CP_h$. It is proposed that this reversal of hysteresis is due to polymer-polymer interactions that occur in solution at higher concentration, resulting in further entropy loss upon unfolding of the polymer chains upon hydration as compared with lower concentration, where the hydrated polymers have less interaction in solution. The decrease in transition temperatures that is observed at 0.1 wt-% polymer concentration in 50 wt-% ethanol implies an increased solubility of the PMMA, which is not understood at this moment.

Besides the UCST behaviour of PMMA in aqueous ethanol solutions, the solubility of PMMA-14k was investigated in aqueous methanol and isopropanol solutions, also revealing UCST transitions, as demonstrated in Fig. 5. The hydrogen bonding strength of the alcohols decreases in the order methanol, ethanol, and isopropanol, strongly affecting the solvation of water molecules in the corresponding alcohol/water mixtures. In fact, the water hydrogen bonded structure is hardly formed in aqueous isopropanol solutions with 70 mol-% isopropanol indicating the presence of single, non-clustered water molecules.[26] In contrast, for 70 mol-% methanol in water only a small fraction of water is present as non-clustered species.[27,28] This difference is also reflected in the UCST behaviour of PMMA-14k in these alcohol/water solvent mixtures (Fig. 5). In methanol/water, only slightly improved solubility of PMMA is observed upon addition of water to methanol, which is most likely due to hydration of the esters groups. However, $CP_c$ is always higher than $CP_h$ due to the presence of water clusters in the solvent mixture compensating the favourable polymer hydration enthalpy, which is comparable to the previously discussed PMMA solubility behaviour in ethanol/water mixtures with less than 60 wt-% ethanol. The PMMA solubility in aqueous isopropanol solutions showed very similar behaviour as in aqueous ethanol solutions, whereby the
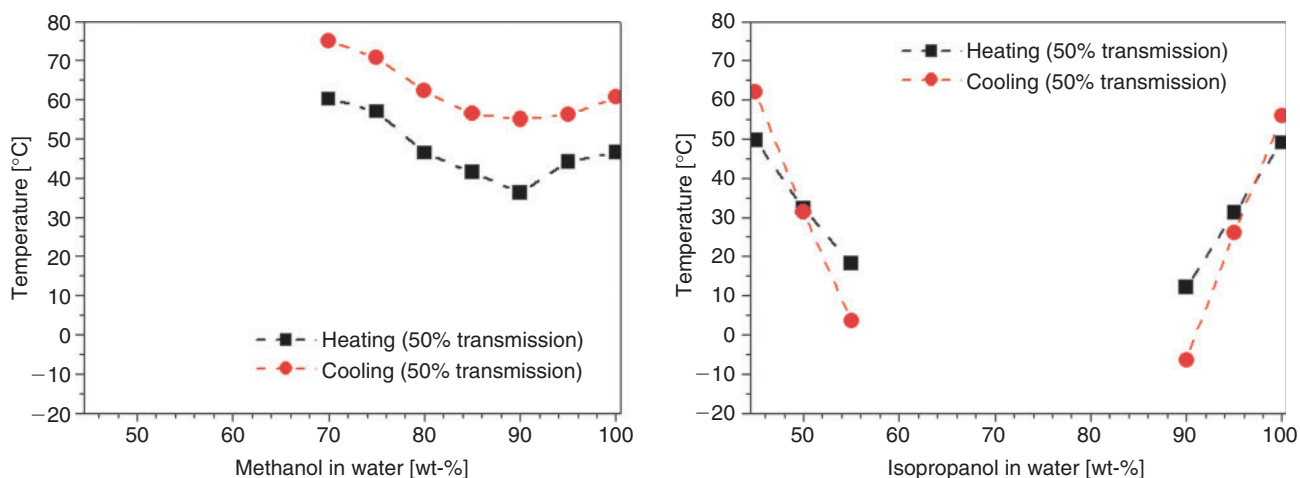
**Fig. 5.** Clearance points upon heating and cloud points upon cooling as a function of alcohol content in 0.5 wt-% aqueous solutions of PMMA-14k. Left: methanol/water mixtures; right: isopropanol/water mixtures.
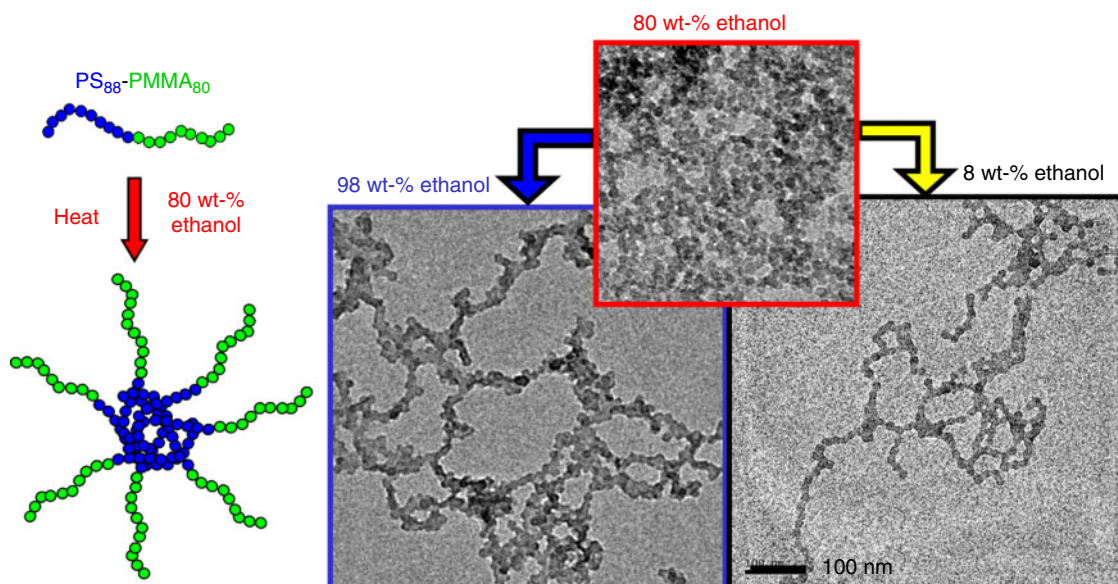


**Fig. 6.** Left: Schematic representation of the micellization of PS-PMMA in 80 wt-% aqueous ethanol. Right: Transmission electron micrographs of PS-PMMA micelles (0.2 wt-%) in aqueous solutions containing 80 wt-% ethanol (top, middle), 98 wt-% ethanol (left), and 8 wt-% ethanol (right). The latter two micellar solutions (0.02 wt-%) were obtained by adding 100 μL of the 80 wt-% ethanol solution into 900 μL of ethanol or water, respectively. The scale bar is valid for all TEM images.

effect of water is more pronounced and the optimal solvent mixture is shifted to ∼70 wt-% isopropanol. Both these observations nicely correspond to the weaker hydrogen bonding network in isopropanol as well as the presence of single, non-clustered water molecules in aqueous 70 mol-% isopropanol.[25]

The importance of the discussed solubility of PMMA in alcohol/water solvent mixtures was previously demonstrated by the formation of core-shell micelles of double-hydrophobic PS-PMMA block copolymers (Fig. 6, left).[15] Obviously, the use of low-toxicity ethanol/water solvent mixtures is preferable over the commonly applied organic solvents for the micellization of such double hydrophobic block copolymers. However, it would be even more desirable to have such micellar particles in almost pure water or ethanol to prevent precipitation due to variation in solvent composition. Therefore, preliminary attempts were performed to transfer the PS-PMMA micelles from aqueous 80 wt-% ethanol solution into water or ethanol. Diluting a

0.2 wt-% PS-PMMA micellar solution 10 times into water or ethanol resulted in clear and stable 0.02 wt-% micellar solutions in aqueous 8 or 98 wt-% ethanol, respectively. These micellar solutions remained stable for at least several weeks after which time the solutions were no longer examined. TEM analysis of these solutions revealed in all cases spherical micelles with 15–16 nm average collapsed diameter in the dry state (Fig. 6, right), whereby it should be noted that the hydrated size in solution might be different due to possible partial collapse of the corona upon transfer. Unfortunately, this could neither be confirmed with cryoTEM nor with dynamic light scattering due to the very low micelle concentration. In addition, the micelles appear to form chains in TEM after transfer to both water and ethanol, whereby it is not clear whether these chains are also present in solution or that it is a drying effect during sample preparation. Attempts to increase the concentration of the parent solution with 80 wt-% ethanol resulted in precipitation of

the micelles upon transfer to ethanol or water indicating that 0.02 wt-% is the maximum achievable concentration in water and ethanol. Nonetheless, these are the first reported examples of stable PS-PMMA micellar solutions in almost pure water or ethanol. It is important to note that reference experiments to directly dissolve 0.02 wt-% PS-PMMA in 8 and 98 wt-% ethanol solutions did not result in the formation of micelles upon heating, i.e. only insoluble polymer particles remained, demonstrating the importance of preforming the micelles in 80 wt-% ethanol, followed by transfer to water or ethanol.

## Conclusions

The improved solubility and thermoresponsive behaviour of PMMA in alcohol/water solvent mixtures is discussed in detail. The PMMA phase transition temperature in ethanol/water increases with increasing molar mass and polymer concentration as determined by cloud point measurements. The effect of molar mass was ascribed to an increased entropy loss upon unfolding of a larger polymer globule while the concentration effect is due to an increased interaction between the polymer chains in solution. Evaluation of the hysteresis between dissolution upon heating and precipitation upon cooling revealed that $CP_c > CP_h$ for aqueous ethanol solutions with <60 wt-% or >90 wt-% ethanol, while $CP_h > CP_c$ for intermediate ethanol fractions. This peculiar behaviour was hypothesized to be related to the enthalpy gain by hydration of the polymer ester bonds in comparison to single, non-clustered water molecules present at intermediate ethanol contents. Extending this hypothesis to aqueous methanol and isopropanol solutions of PMMA indeed revealed only a slightly improved solubility in aqueous methanol where almost no single water molecules are present and even stronger improved PMMA solubility in aqueous isopropanol compared with aqueous ethanol, due to an even larger fraction of non-clustered water molecules. Finally, preliminary results were presented demonstrating the possibility to transfer PS-PMMA micelles from an aqueous 80 wt-% ethanol solution to almost pure water and ethanol solutions as evidenced by TEM analysis.

As demonstrated by the final micellization results, these new insights into the PMMA solubility in ethanol/water solvent mixtures open up new avenues for polymer processing as well as polymer self-assembly concepts.

## Acknowledgement

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