Spectroscopic Studies of Behaviour and Interactions in PVME/Water Mixtures

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Abstract. Aqueous solutions of poly(vinyl methyl ether) are known to undergo phase separation in dependence of temperature. The differential scanning calorimetry (DSC), high-resolution nuclear magnetic resonance (NMR) and optical microscopy (OM) methods have been used to study dynamical and structural changes during the phase separation. Results show strong dependence of DSC, NMR and OM parameters on polymer concentration and non-reversibility during heating and subsequent cooling process in the short time range. NMR data were used to construct van 't Hoff plots and changes of the enthalpy and entropy characterizing the phase transition were determined.

Introduction

Poly(vinyl methyl ether) (PVME) in aqueous solutions has low critical solution temperature (LCST) around 308 K. Below LCST there is one homogeneous phase and above LCST the solution is turbid and separates into two phases [1, 2] as schematic Figure 1 shows. Phase separation is a consequence of the coil-globule transition on the molecular level and it is followed by aggregation, as it was shown for acrylamide-based polymers in water by light scattering and small neutron scattering [3–7]. Better insight to the phase transition in PVME/water solutions brought cloud point, calorimetric, viscometric, viscoelastic, infrared and Raman measurements [1, 2, 8–15]. Maeda [16] determined three PVME concentration regions differing in number of water molecules forming a complex with PVME. The phase diagram was revealed for PVME aqueous solutions from modulated temperature differential scanning calorimetry (DSC) experiments [14, 17, 18].

In the past we used ^{1}H nuclear magnetic resonance (NMR) spectroscopy to describe microscopic changes during temperature-induced phase separation in PVME/D_2O solutions [19–24]. The phase separation above the LCST could be seen in the NMR spectra by broadening of the peak corresponding to PVME globular units. In this case rather compact globular-like structures are formed [19, 20]. In the range of polymer concentrations 0.1–30 wt.% above the phase separation, the fraction of PVME units involved in globular-like structures is approximately 0.85 [20].

Van 't Hoff plot was constructed and thermodynamic parameters of the separation in polymer solutions and hydrogels were determined from NMR data [25–27]. Using phenomenological model of macromolecules consisting of independent cooperative units, cooperativity of the transition can be calculated from comparison of the effective enthalpy of van 't Hoff and the calorimetric enthalpy of a polymer molecule as determined by DSC [28, 29].

In this work we studied the thermodynamics of the phase separation in PVME/water solution using calorimetric and NMR experiments. Reversibility of the separation process was documented by DSC thermograms and optical microscopy (OM).
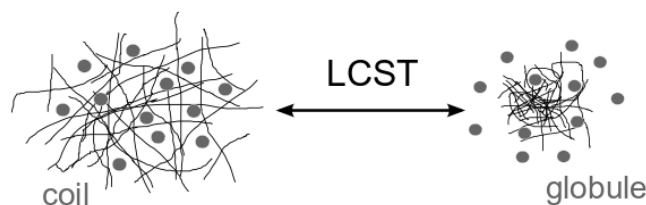

Figure 1. Schematic description of phase separation of polymer in aqueous solution.

Experimental details

For all measurements the 50 wt.% PVME/water solution was used (M_w = 60500 g/mol, M_w/M_n = 3, purchased from Aldrich). PVME has been dried up and then aqueous solutions were prepared in a concentration range of polymer 1–90 wt.%. Only for the NMR measurements deuterated water was added instead of pure water. High-resolution ^{1}H NMR spectra were obtained with a Bruker Avance 500. Before each experiment, the samples were kept at the experimental temperature always for 15 min. Optical microscope Nikkon 30 was utilized for OM experiments and samples were heated from 298 to 323K by the rate 1K/min and then cooled down to the room temperature. DSC measurements were performed with a Pyris apparatus (Perkin-Elmer), one complete cycle with heating and cooling rate 10 K/min within a range 298–318 K was carried out.

Results and discussion

Differential Scanning Calorimetry

Heating thermograms for different PVME concentrations are seen in Figure 2. It is obvious that the shape of the DSC peaks depends on polymer concentration. While temperature onset (which defines the origin of the transition) is not practically influenced by PVME concentration, the enthalpy values given as the peak area show maximum for polymer concentration ≈ 40 wt.% and this is in accord with literature [2, 9].

Figure 3 depicts the heating and cooling branch of one cycle corresponding to formation and dissolving mesoglobules, respectively. It is clearly seen that during cooling the peak is shifted to lower temperatures and shows smaller enthalpy values in comparison with heating. That means that not the same amount of water excluded from coils during globule formation (heating) is incorporated back when the globules are dissolved (cooling), at least in the time scale of minutes.

To characterize non-reversibility of the solution demixing and remixing we plotted concentration dependence of the enthalpy differences between heating and consecutive cooling (Figure 4). Enthalpy was obtained as the integral of the normed thermogram at the intersection points of tangents to the
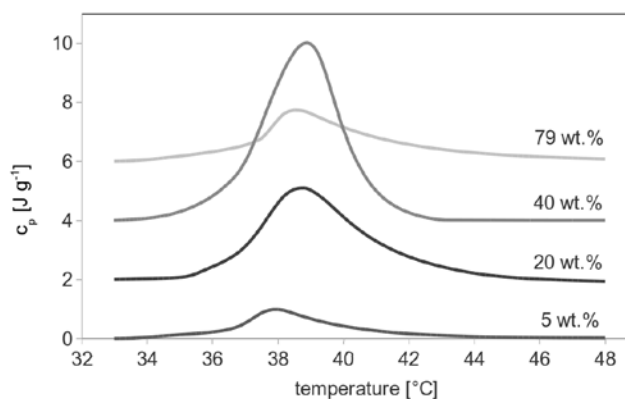

Figure 2. Heating DSC thermograms for various polymer concentrations. Curves are shifted vertically for clarity.
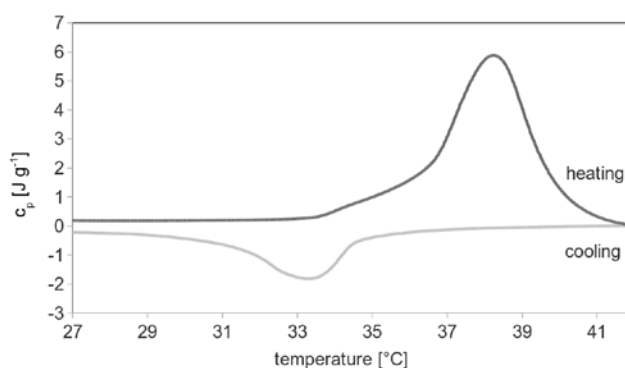

Figure 3. DSC thermogram for one complete cycle for 50 wt.% of PVME.

curve. As the heating and cooling rate was the same we can deduce that the process of separation is much more faster than the dilution process as all the difference values are positive. Remixing process when globules are dissolved is thus more demanding on time as it is a transition from heterogeneous to homogeneous state. Originally free water molecules have to penetrate into the globules and at the same time new hydrogen bonds have to be established. The slowest dilution process and the highest difference corresponds to samples with PVME concentrations 20–30 wt.%.

Another interesting property could be seen if we draw the differences of the onset temperature corresponding to heating and cooling (Figure 5). If we observe samples with low or high polymer concentrations, the process of separation or/and remixing starts at the same temperature. In the middle part of the concentration region there is a maximum around 50–60 wt.%. This concentration region agrees with literature [9] as the region of maximal interaction between water and polymer.

Optical Microscopy

Approximate average size of the polymer globules formed above LCST should be estimated as 2–4 µm (see the OM image obtained at 37 °C in Figure 6). The temperature evolution of images of optical microscope in Figure 6 demonstrates formation of globules during heating and consequently the homogeneous solution becomes turbid. Once heated the system is unable to set original equilibrium in the time comparable to heating/cooling rate and the unmelted cores occur after the heating even if the temperature is reduced below the LCST (33 °C). This is in agreement with DSC measurements where unmelted centers implicate lower values of enthalpy during cooling in comparison with heating.
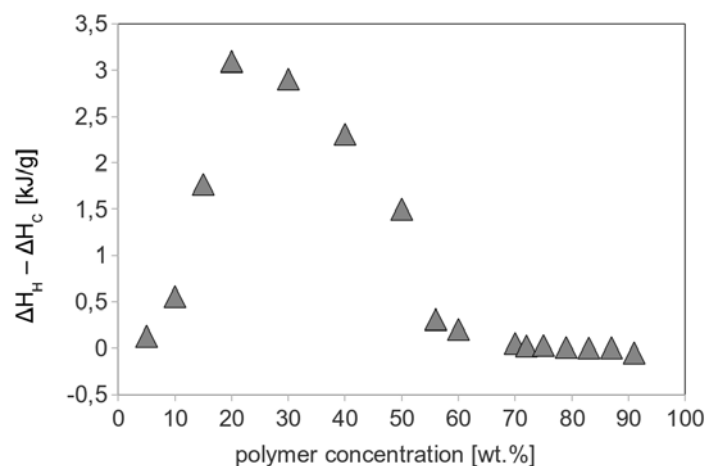

Figure 4. Polymer concentration dependence of the enthalpy differences as obtained from heating and cooling process.
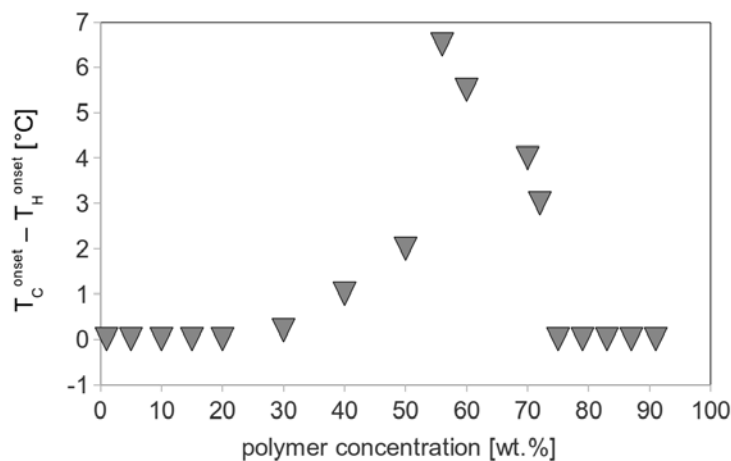

Figure 5. Polymer concentration dependence of the onset temperature differences as obtained from heating and cooling process.
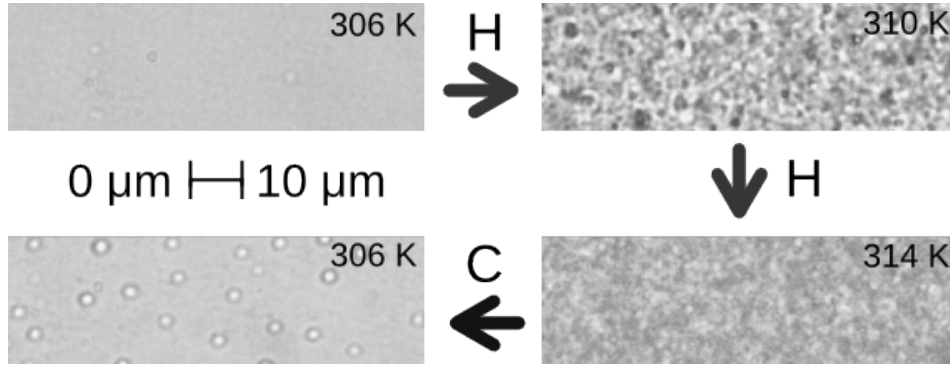
Figure 6. OM images of 85 wt.% PVME/water solution at 306 K, 310 K, 314 K during heating and at 306 K after cooling.
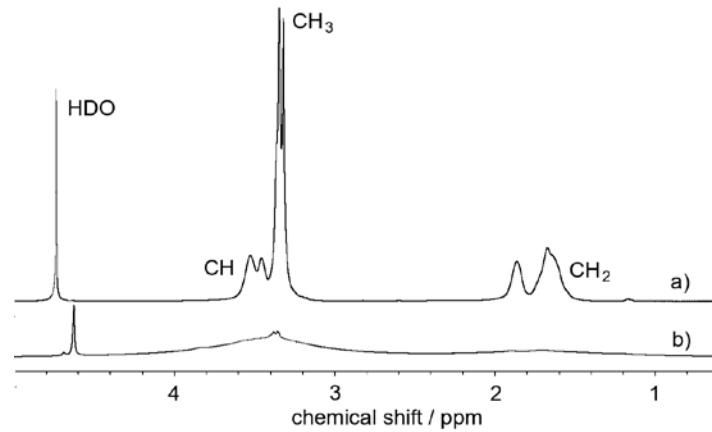

Figure 7. ^{1}H NMR spectra for 30 wt.% PVME a) before and b) after the phase transition.

Nuclear Magnetic Resonance

High-resolution ^{1}H NMR spectra of PVME/D$_2$O solution (c = 30 wt%) measured at two different temperatures are shown in Figure 7. The most observable effect is a substantial decrease in the integrated intensity of all PVME bands due to the pronounced reduction in mobility polymer units involved in compact globular structures.

From the temperature dependent integral intensity, parameter p could be obtained as:

$$p = \frac{I}{I_0} \tag{1}$$

where I and I_0 are in general terms integrated intensity of polymer peak in the partly phase-separated system and before phase separation occurs, respectively. Quantity p signifies the fraction of the phase separated polymer units with reduced mobility above LCST. Considering the phase separation as the competition between non-phase separated (coil) and phase separated (globule) states governed by the Gibbs free energy than the equilibrium constant K is given by the ratio [25]:

$$K = \frac{p}{1-p} \tag{2}$$

Van 't Hoff equation describes temperature changes of the equilibrium constant K of the coil-globule transition as follows:

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{3}$$

where ΔH and ΔS are the changes in enthalpy and entropy, respectively, and R is the gas constant. The dependences of R $\ln(p/(1-p))$ on $-1/T$ for the solutions PVME with various polymer concentrations are shown in Figure 8.
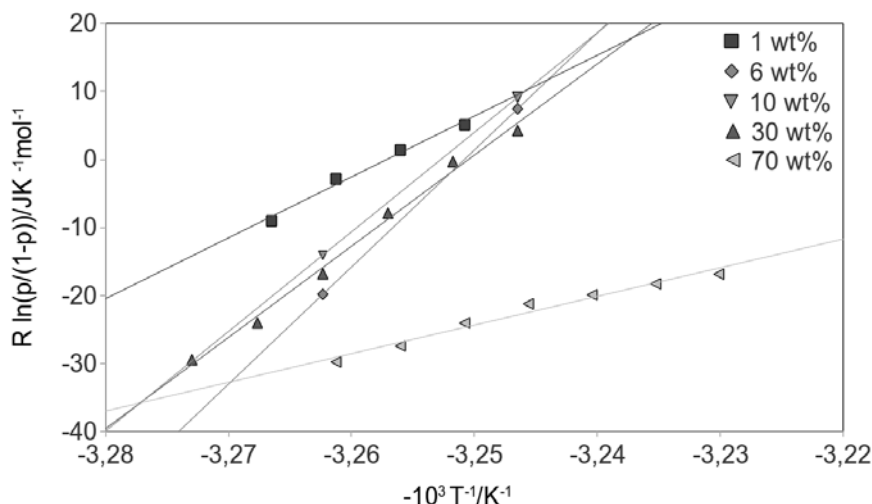
Figure 8. The van 't Hoff plot for the phase transition in PVME solutions with various polymer concentrations. Solid lines are fits according to eqs 2 and 3.

ΔH_{NMR} values obtained as the slopes of linear dependences in Figure 8 can be compared with enthalpy changes ΔH_{DSC} from DSC. For solutions with PVME concentrations 1–30 wt.% the obtained value $\Delta H_{NMR} \approx 1.5$ MJ/mol and $\Delta H_{DSC} \approx 4.4$ kJ/mol (monomer unit). Assuming that the phase transition is a cooperative process and the polymer chain consists of cooperative units (domains) which undergo transition as a whole [28, 29], the values ΔH_{NMR} are thus related to mol of cooperative units. From the ratios $\Delta H_{NMR}/ \Delta H_{DSC}$ the number of monomer units in one domain can be determined as ≈ 330. This means that the size of domains agrees quite well with average degree of polymerization (DP ≈ 348) so showing that in this case the cooperative unit is the whole polymer chain.

Conclusion

In this work we investigated microscopic phase separation in aqueous solutions of PVME using NMR, DSC and OM methods. These methods were chosen to obtain information for determination of the critical temperature and enthalpy changes, reversibility and microscopic morphology during phase separation events. DSC and OM results showed non-reversible character of the phase separation particularly for polymer concentrations 30–50 wt.% as a consequence of different dynamical and structural changes during formation and dissolving of mesoglobules.

In addition, NMR temperature dependence measurements could be used to calculate the separated fraction of polymers above the LCST. Van 't Hoff plot then provide deeper insight into the thermodynamical properties of the transition such as enthalpy and entropy changes. Moreover with parallelly obtained DSC data, the cooperativity character of the phase transition could be investigated.

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