

# RHEOLOGICAL AND IR SPECTROSCOPIC STUDY ON PHASE SEPARATION OF POLY (VINYL METHYL ETHER) (PVME) AQUEOUS SOLUTION: EFFECT OF SPHERICAL NANOPARTICLES ON PHASE DIAGRAM

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In this study the phase diagram of Poly(Vinyl Methyl ether)(PVME) aqueous solution in the presence and absence of hard spherical hydrophilic nanoparticles was determined during heating and cooling by using rheological measurements, modulated temperature differential scanning calorimetry (MTDSC), optical microscopy and FT-IR. The viscoelastic properties of PVME/water solution were investigated in oscillatory shear above and below the lower critical solution temperature (LCST). The “coil-globule” transition which results in the abrupt increase in the elastic modulus by heating of the solution above the LCST, is due to competition between PVME hydrophilic ether groups (which stabilize the solution by hydrogen bonds formation) and PVME hydrophobic methyl groups (which destabilize the solution by changing the water structure). The morphological evolution has been investigated in two phase region by the optical microscopy in temperature sweep mode. We further studied the influence of the interactions on infrared band shift for  $\nu_s(CH_3)$  and  $\nu(C - O)$  as a function of concentration. The infrared band frequencies of the two modes versus the concentration of PVME in aqueous solution have been plotted; a bending point and also two slopes have been founded. Peak positions of  $\nu_s(CH_3)$  band shifted to a lower wavenumber and those of the  $\nu(C - O)$  band shifted to a higher wavenumber with increase in the concentration. Larger shifts of the peak positions above the critical concentrations (bending points) indicate transitions in the hydration states of the corresponding groups. In order to investigate the interaction changing during phase separation, FT-IR was carried out below and above the LCST temperature in different samples. Positions of the  $\nu_s(CH_3)$  band were nearly independent of PVME concentration above the LCST, indicating that most of the methyl groups were dehydrated. The time lag observed through remixing of the solution sample during cooling process was observed by rheological and thermal analysis, which was attributed to the interchain and intrachain quasi hydrogen bonds between different chain segments. The influence of hard spherical hydrophilic nanoparticles (fumed silica) on the phase behavior of PVME aqueous solution has been investigated. According to rheological measurements, the phase separation take place more rapidly as the result of competition between nanoparticles and PVME chains to form hydrogen bonds with water which reduce the PVME intra and inter hydrogen bonding and weaken the solution stability. Furthermore, based on FT-IR results in the presence/absence of nanoparticles, the formation of new hydrogen bond between PVME chains entangled on nanoparticles with water molecules has been founded.