

## ABSTRACT

In the present work, the effect of counterion valency and the ionic strength of the solution ( $I$ ) on the association phenomena in aqueous solutions of poly ( $\alpha$ -alkylcarboxylic acids) at room temperature and during heating and cooling was studied by various techniques.

By dynamic (DLS) and static light scattering (SLS) the formation of nanoparticles of two poly(methacrylic acid) (PMA) isomers, atactic (aPMA) and isotactic (iPMA), was investigated in aqueous solutions of inorganic metal multivalent (NaCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, and LaCl<sub>3</sub>) and organic hydrophobic monovalent (tetramethylammonium (TMACl), tetraethylammonium (TEACl) and tetrapropylammonium (TPACl)) chlorides. iPMA associates are stable at a much higher degree of neutralization ( $\alpha_N$ ) of carboxylic groups ( $\alpha_N \approx 0,20$ ) than aPMA associates ( $\alpha_N = 0$ ), indicating a stronger intermolecular association between iPMA chains. The PMA associates in the presence of inorganic metal counterions have the characteristics of microgel particles with a denser core and a swollen corona. According to the values of shape parameter ( $\rho$ ) ( $\rho \approx 0,90$ ), both isomers behave differently in the presence of Mg<sup>2+</sup> than in the presence of Na<sup>+</sup>, Ca<sup>2+</sup> and La<sup>3+</sup>. Associates formed in the presence of Mg<sup>2+</sup> thus have a more even mass distribution (without a clear formation of a core-shell structure) in comparison with those in the presence of Na<sup>+</sup>, Ca<sup>2+</sup> and La<sup>3+</sup>, which are characterized by lower values of  $\rho$  ( $\approx 0,70-0,80$ ). This was attributed to the strong hydration of Mg<sup>2+</sup> ions, resulting in Mg<sup>2+</sup> ions favoring monodentate binding to carboxylic (COOH)/carboxylate (COO<sup>-</sup>) groups. Ca<sup>2+</sup> and La<sup>3+</sup> ions, on the other hand, bind more strongly and in a bidentate manner. Differences in the structure of associates in the presence of multivalent cations are also reflected in different dependences of ionization enthalpies ( $\Delta H_{ion}$ ) on  $\alpha_N$ , and also in different results of fluorimetric and pH measurements. Microgel-like particles are also formed by both PMA isomers in the presence of TMA<sup>+</sup>. These organic cations interact with COOH/COO<sup>-</sup> groups directly through electrostatic interactions, while the binding of larger and more hydrophobic TEA<sup>+</sup> and TPA<sup>+</sup> to PMA chains is dominated by hydrophobic type of interactions. As a result, these particles are more swollen and loosened ( $\rho \approx 0,90$ ). Meanwhile, the structure of iPMA associates is more elongated in the presence of larger counterions TEA<sup>+</sup> and TPA<sup>+</sup> due to their ability to hinder iPMA main chains from getting into contact with one another, thus preventing the more extensive aggregation of polyions.

By several experimental techniques (visual experiment, UV-Vis spectroscopy, DLS and SLS, calorimetry, fluorimetry, NMR), it was clearly shown that the temperature-induced intermolecular association of a- and iPMA in aqueous solutions in the presence of inorganic metallic multivalent and organic hydrophobic monovalent counterions displays an opposite thermoresponsiveness. In the case of aPMA, association and phase separation take place during

heating (so-called lower critical solution temperature behaviour; LCST). The resulting aPMA precipitate dissolves in the presence of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  during cooling, while the aggregation is irreversible in the presence of  $\text{La}^{3+}$ . In contrast to aPMA, iPMA associates disintegrate completely or partially upon heating the solutions without macroscopic phase separation (so-called upper critical solution temperature behaviour; UCST). De-association is completely reversible. Increase in the  $I$  of  $\text{NaCl}$ ,  $\text{MgCl}_2$ , and  $\text{CaCl}_2$  solutions leads to a decrease in the LCST values, whereas in the case of  $\text{LaCl}_3$ , an increase in  $I$  has no significant effect on LCST. aPMA solutions in the presence of hydrophobic cations also display a LCST behaviour. When  $\text{TMA}^+$  cations are present in the solution, the aPMA precipitate formed during heating dissolves upon cooling, while this is not the case in  $\text{TEACl}$  and  $\text{TPACl}$  solutions. With increasing length of the nitrogen-bound alkyl chains, and thus the hydrophobicity of the cation, the LCST values for aPMA solutions decrease. Meanwhile, organic cations induce irreversible disintegration of iPMA associates in aqueous solutions during heating.

A more hydrophobic analogues of poly ( $\alpha$ -alkylcarboxylic acids), poly (ethacrylic acid) (PEA) and poly (propylacrylic acid) (PPA), in the presence of inorganic metal multivalent cations  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{La}^{3+}$  form associates with a more swollen structure and evenly distributed mass throughout the particle in comparison with the ones formed by a- and iPMA due to longer and sterically more demanding hydrophobic ethyl and propyl side groups located inside the particles. These findings were also supported by DLS and SLS results ( $\rho \approx 1,0$ ) and fluorimetric measurements. Like aPMA, also PEA and PPA display LCST behaviour. The association of PEA and PPA in the presence of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{La}^{3+}$  is irreversible. Phase separation occurs on both, the macroscopic level (in the presence of divalent  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) in the form of a gel-like precipitate, as well as on the mesoscopic level (in the presence of  $\text{Na}^+$  and  $\text{La}^{3+}$ ), when solutions become merely opaque or fine precipitate is formed. This is due to the formation of strong hydrogen bonds  $\text{COOH}\cdots\text{COO}^-$  on different polymer chains. Because the solvent quality is worsened during heating, these  $\text{COOH}\cdots\text{COO}^-$  bonds become more and more favored and get in addition even stronger during cooling. As a result, stable associates of PEA and PPA are formed.

The lengthening of hydrophobic alkyl side groups of the investigated aPMA, PEA, and PPA strongly influences their behaviour in aqueous solutions. Weaker polyacid has longer and more hydrophobic side group (methyl < ethyl < propyl) and forms stronger hydrogen bonds  $\text{COOH}\cdots\text{COO}^-$  due to a more pronounced positive inductive effect. The hydrogen bonds in the pair  $\text{COOH}\cdots\text{COO}^-$  that form between PEA and PPA chains are thus stronger than the hydrogen bonds in the pair  $\text{COOH}\cdots\text{COOH}$  that form between aPMA chains and ensure the stability of the associates formed during heating.