

1. Raziskovalna organizacija (*Research organisation*):

Univerza v Ljubljani, Fakulteta za kemijo in kemijsko tehnologijo
University of Ljubljana, Faculty of Chemistry and Chemical Technology

2. Ime in priimek mentorja (*Name and surname of a mentor*):

Ksenija Kogej

3. Področje znanosti iz šifranta ARRS (*Primary research field*):

1.04.01 Naravoslovje/Kemija/Fizikalna kemija
1.04.01 Natural Sciences/Chemistry/Physical Chemistry

4. Kontaktni e-naslov mentorja (*Contact of a mentor*):

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5. Kratek opis programa usposabljanja (*Short description of the program*):

SLO

Študent/ka bo v okviru uposabljanja v jeseni leta 2016 vpisal/a Doktorski študij Kemijskih znanosti na Univerzi v Ljubljani, Fakulteta za kemijo in kemijsko tehnologijo, UL-FKKT, ter pričel/a z raziskovalnim delom na tematiki z naslovom "Polimerni nanodelci na osnovi poli(α -alkil karboksilnih kislin)" pod mentorstvom prof. dr. Ksenije Kogej na UL-FKKT, Katedra za fizikalno kemijo.

Polimerni nanodelci (PNP) so zanimivi za študij zaradi številnih možnosti uporabe na raznih področjih znanosti in tehnologije. Za njihovo tvorbo se uporabljajo številni pristopi, ki jih lahko razdelimo na kemijske in fizikalne. Fizikalni pristopi vključuje med drugim tudi združevanje homopolimerov v agregate/asociate na osnovi fizikalnih interakcij, na primer vodikovih vezi in hidrofobnega efekta.

Namen tega dela je pripraviti stabilne in vodotopne nanodelce iz raznih poli(α -alkilkarboksilnih kislin) (PACA) na osnovi asociacije/agregacije med polimernimi verigami. Uporabili bomo poli(metakrilno), PMA, poli(etilakrilno), PEA, in poli(propil akrilno kislino), PPA. Z naraščajočo hidrofobnostjo stranske alkilne verige na α -C atomu topnost teh polikarboksilnih kislin v vodi pada. Pri stopnji ionizacije $\alpha = 0$ je v vodi topna le ataktična oblika PMA, aPMA, medtem ko se izotaktična PMA, iPMA, ne raztopi.

Tudi PEA in PPA nista topni, ne glede na njuno taktičnost. Te PACA se raztopijo, ko COOH skupine ioniziramo z dodakom luga, a se potem ponovno oborijo, če jih nazaj protoniramo, pri čemer v ozkem območju pH (na primer nad $\alpha \approx 0,2$ za iPMA) tvorijo topne medmolekulske asociate z dimenzijami v nano-območju, torej nanodelce (NP). Namen tega dela je doseči solubilizacijo omenjenih hidrofobnih polimerov že pri $\alpha = 0$ v obliki ND, v katere bi lahko potencialno vgradili hidrofobne topljence. Za pripravo popolnoma ioniziranih oblik PACA ($\alpha = 1$) bomo uporabili razne amonijeve hidrokside z različno hidrofobno naravo kationa: tetrametil amonijev hidroksid, TMAOH, tetraetil amonijev hidroksid, TEAOH, in holin hidroksid, ChOH. ChOH je znan kot superbaza, ki je za ionizacijo celo bolj učinkovit od NaOH. Z dodatkom HCl bomo nato stopnjo ionizacije znižali nazaj na/proti $\alpha = 0$ in zasledovali tvorbo NP ter eventualno obarjanje. Spreminjali bomo tudi ionsko jakost raztopin, tako da jim bomo dodali razne kloride v različnih koncentracijah: tetrametil amonijev klorid, TMACl, tetraetil amonijev klorid, TEACl, in holin klorid, ChCl ter nekatere ionske tekočine na osnovi metilimidazola, na primer etil-metilimidazolijev klorid (EMIMCl), butil-metilimidazolijev klorid (BMIMCl) in heksil-metilimidazolijev klorid (HMIMCl). Metode, ki jih bomo uporabili za študij, bodo UV in fluorescenčna spektroskopija, kalorimetrija, statično (SLS) in dinamično sipanje svetlobe (DLS) in druge. Zanimal nas bo še vpliv temperature na tvorbo in obstojnost ND, zato bomo uporabili tudi diferenčno dinamično kalorimetrijo ter študirali lastnosti agregatov z SLS in DLS še v odvisnosti od temperature.

ANG

The student will enrol in the PhD program Chemical Sciences at the University of Ljubljana, Faculty of Chemistry and Chemical Technology, UL-FCCT, and start the research work at UL-FCCT, Chair for Physical Chemistry, on the topic "*Polymeric nanoparticles on the basis of poly(α -alkyl carboxylic acids)*" under the supervision of prof. dr. Ksenije Kogej.

The interest in polymeric nanoparticles (PNP) comes from numerous applications of PNPs in various scientific and technological fields. There are many approaches for PNPs formation, which can be divided into chemical and physical. Physical approaches include, among others, also self-assembly of homopolymers into aggregates/associates through physical interactions, e.g. hydrogen bonds and hydrophobic effect. The purpose of this work is to prepare stable and water soluble nanoparticles (NPs) from various poly(α -alkyl carboxylic acids), PACAs, through association/aggregation of several polymer chains. The following PACAs will be used: poly(methacrylic acid), PMA, poly(ethacrylic acid), PEA, and poly(propylacrylic acid), PPA. The solubility of these PACAs in water decreases with increasing hydrophobicity of the alkyl side chain on the α -C atom. Only the atactic PMA, aPMA, dissolves at a degree of ionization zero, $\alpha = 0$, whereas the isotactic form, iPMA, is not soluble at $\alpha = 0$. The same holds for the other two, i.e. PEA and PPA, irrespective of their tacticity. The polyacids dissolve when carboxyl, COOH, groups are ionized and precipitate again when they are protonated. During protonation, they form water soluble intermolecular associates/aggregates (NPs) in a narrow pH region somewhat above $\alpha \approx 0,2$ (for iPMA). The aim of this work is to solubilize the "hydrophobic" PACAs already at $\alpha = 0$ in the form of NPs that could serve for incorporation of hydrophobic molecules. The completely ionized PACAs (at $\alpha = 0$) will be prepared by using various ammonium hydroxides with a different degree of hydrophobicity of the cation: tetramethyl ammonium hydroxide (TMAOH), tetraethyl ammonium hydroxide (TEAOH) and choline hydroxide (ChOH). Choline hydroxide is known as a superbases, being even more efficient than NaOH. The degree of ionization will be decreased by the addition of HCl to/towards $\alpha = 0$ and the formation of NPs will be followed. The ionic strength of the solutions will be varied by adding various chlorides at different concentrations: tetramethyl ammonium chloride (TMACl), tetraethyl ammonium chloride (TEACl), choline chloride (ChCl) and ionic liquids on the basis of methyl imidazolium, for example ethyl-methylimidazolium chloride (EMIMCl), buthyl-methylimidazolium chloride (BMIMCl) in hexyl-methylimidazolium chloride (HMIMCl). To study the aggregation process, the following methods will be used: UV and fluorescence spectroscopy, calorimetry, static (SLS) and dynamic light scattering (DLS) and others. The effect of temperature on NPs formation and stability will be followed as well. For this purpose, we will use the differential scanning calorimetry (DSC) and study properties of aggregates by SLS and DLS in dependence on temperature.