

**UNIVERZITET U BEOGRADU
TEHNOLOŠKO-METALURŠKI FAKULTET
NASTAVNO-NAUČNOM VEĆU**

Predmet: Referat o urađenoj doktorskoj disertaciji kandidata Alise Zlatanić

Odlukom Nastavno-naučnog veća Tehnološko-metalurškog fakulteta Univerziteta u Beogradu br. 35/77 od 07.03.2019. godine, imenovani smo za članove Komisije za pregled i ocenu doktorske disertacije kandidata Alise Zlatanić, magistra tehničkih nauka, pod naslovom

„Uticaj strukture cikličnih monomera na tok anjonske polimerizacije i svojstva vinil-terminiranih polisiloksana“

„The Effect of Structure of Cyclic Monomers on the Course of Anionic Polymerization and Properties of Vinyl-Terminated Polysiloxanes“

Posle pregleda dostavljene disertacije i drugih pratećih materijala i razgovora sa kandidatom, Komisija podnosi sledeći

R E F E R A T

1. UVOD

1.1. Hronologija odobravanja i izrade disertacije

- Školske 2016/2017 – Kandidat Alisa Zlatanić, magistar tehničkih nauka, je upisala III godinu doktorskih akademskih studija na Tehnološko-metalurškom fakultetu Univerziteta u Beogradu, profil Hemija.
- 15.03.2018. - Kandidat Alisa Zlatanić je prijavila temu za izradu doktorske disertacije na Tehnološko-metalurškom fakultetu, Univerziteta u Beogradu, pod nazivom „Uticaj strukture cikličnih monomera na tok anjonske polimerizacije i svojstva vinil-terminiranih polisiloksana (The Effect of Structure of Cyclic Monomers on the Course of Anionic Polymerization and Properties of Vinyl-Terminated Polysiloxanes)“.
- 29.03.2018. - Na sednici Nastavno-naučnog veća Tehnološko-metalurškog fakulteta Univerziteta u Beogradu doneta je odluka (broj 35/92) o imenovanju članova Komisije za ocenu podobnosti teme i kandidata Alise Zlatanić, magistra tehničkih nauka, pod predloženim nazivom „Uticaj strukture cikličnih monomera na tok anjonske polimerizacije i svojstva vinil-terminiranih polisiloksana (The Effect of Structure of Cyclic Monomers on the Course of Anionic Polymerization and Properties of Vinyl-Terminated Polysiloxanes)“.
- 26.04.2018. - Na sednici Nastavno-naučnog veća Tehnološko-metalurškog fakulteta Univerziteta u Beogradu doneta je odluka (broj 35/161) o prihvatanju Referata Komisije za ocenu podobnosti teme i kandidata Alise Zlatanić, magistra tehničkih nauka, za izradu

doktorske disertacije pod predloženim nazivom „Uticaj strukture cikličnih monomera na tok anjonske polimerizacije i svojstva vinil-terminiranih polisiloksana (The Effect of Structure of Cyclic Monomers on the Course of Anionic Polymerization and Properties of Vinyl-Terminated Polysiloxanes)“. Za mentora je imenovana dr Marija Nikolić, van. prof. Tehnološko-metalurškog fakulteta Univerziteta u Beogradu.

- 28.06.2018. - Na sednici Veća naučnih oblasti prirodnih nauka data je saglasnost (broj 61206-2265/4-18) na predlog teme doktorske disertacije Alise Zlatanić, magistra tehničkih nauka, pod nazivom „Uticaj strukture cikličnih monomera na tok anjonske polimerizacije i svojstva vinil-terminiranih polisiloksana (The Effect of Structure of Cyclic Monomers on the Course of Anionic Polymerization and Properties of Vinyl-Terminated Polysiloxanes)“.
- 07.03.2019. - Na sednici Nastavno-naučnog veća Tehnološko-metalurškog fakulteta Univerziteta u Beogradu doneta je odluka (br. 35/77) o imenovanju Komisije za ocenu doktorske disertacije Alise Zlatanić, magistra tehničkih nauka, pod nazivom „Uticaj strukture cikličnih monomera na tok anjonske polimerizacije i svojstva vinil-terminiranih polisiloksana (The Effect of Structure of Cyclic Monomers on the Course of Anionic Polymerization and Properties of Vinyl-Terminated Polysiloxanes)“. Komisija za ocenu doktorske disertacije je za predsednika Komisije izabrala dr Ivanku Popović, redovnog profesora Tehnološko-metalurškog fakulteta Univerziteta u Beogradu.

1.2. Naučna oblast disertacije

Istraživanja u okviru ove doktorske disertacije pripadaju naučnoj oblasti Hemijske nauke i užoj naučnoj oblasti Hemija za koju je matičan Tehnološko-metalurški fakultet Univerziteta u Beogradu. Mentor je dr Marija Nikolić, vanredni profesor Tehnološko-metalurškog fakulteta Univerziteta u Beogradu, koja je na osnovu dosadašnjih objavljenih radova i iskustava kompetentna da rukovodi izradom ove doktorske disertacije.

1.3. Biografski podaci o kandidatu

Alisa Zlatanić je rođena 08.04.1967. godine u Pljevljima. Osnovnu školu i gimnaziju je završila u Priboju. Na Tehnološko-metalurški fakultet Univerziteta u Beogradu upisala se školske 1985/86. godine. Diplomirala je 15.02.1993. na smeru Organska hemijska tehnologija i polimerno inženjerstvo odbranom diplomskog rada na temu: „Sinteza i karakterizacija nezasićenih poliestara sa završnim akrilatnim grupama“. Poslediplomske studije na Tehnološko-metalurškom fakultetu Univerziteta u Beogradu upisala je školske 1993/94. godine na smeru Hemija i inženjerstvo polimera. Ispite predviđene planom i programom magistarskih studija položila je sa prosečnom ocenom 9,89. Magistarske studije je završila 20.10.1997. godine odbranivši magistarsku tezu pod nazivom: „Sinteza i reološko ponašanje nezasićenih poliestara sa završnim akrilatnim grupama” sa ocenom 10.

Školske 2016/17 mr Alisa Zlatanić upisala je III godinu doktorskih studija na Tehnološko-metalurškom fakultetu Univerziteta u Beogradu - studijski program Hemija.

Alisa Zlatanić, magistar tehničkih nauka, bila je zaposlena na Tehnološko-metalurškom fakultetu Univerziteta u Beogradu od 06.12.1993. do 31.10.1999. godine, kao asistent-pripravnik na Katedri za opštu i neorgansku hemiju, a zatim kao asistent na istoj Katedri (u zvanje asistenta izabrana je 12.10.1998. godine). Od 1.11.1999. godine do danas je zaposlena

kao viši istraživač saradnik u Centru za istraživanje polimera na Državnom univerzitetu u Pittsburgu, Kansas, SAD (Pittsburg State University, Pittsburg, Kansas).

Oblast naučno-istraživačkog rada mr Alise Zlatanić obuhvata sintezu, karakterizaciju i primenu polimera, kao što su polisiloksani, poliestri, polietri, poliuretani, poliakrilamidi. Značajan deo naučno-istraživačkog rada mr Alise Zlatanić bio je posvećen izučavanju polimera na bazi prirodnih i modelnih triglicerida i njihovoj primeni i komercijalizaciji u oblasti poliuretanskih penastih materijala, adheziva i kompozita. Od početka 2015. godine, mr Alisa Zlatanić je, pod rukovodstvom prof. dr. Petra Dvornića, aktivno angažovana u okviru projekta Državnog univerziteta u Pittsburgu sa kompanijom Honeywell, na istraživanju i razvoju polisiloksana i siloksanskih elastomera, koje je vezano za izradu njene doktorske disertacije.

Kao rezultat celokupnog naučno-istraživačkog rada mr Alise Zlatanić do sada su objavljeni jedno poglavlje u monografiji međunarodnog značaja (M14), 15 radova u međunarodnim časopisima (3 M21a, 7 M21, 3 M22, 2 M23), preko 30 saopštenja na skupovima nacionalnog i međunarodnog značaja, dva patenta i jedan patent je u procesu odobravanja.

Alisa Zlatanić je dobitnik nagrade „Presidential Green Chemistry Challenge Award” za 2007. godinu u kategoriji Dizajna čistijih hemikalija koju je američka Agencija za zaštitu životne sredine dodelila timu istraživača Centra za istraživanje polimera, Državnog univerziteta u Pittsburgu i kompaniji Cargill Inc. za plodotvornu saradnju u razvoju i komercijalizaciji BiOHTM poliola na bazi prirodnih ulja.

Od 2002. godine član je Američkog hemijskog društva.

2. OPIS DISERTACIJE

2.1. Sadržaj disertacije

Doktorska disertacija kandidata Alise Zlatanić pisana je na engleskom jeziku i sadrži 142 strane A4 formata, 58 slika, 16 reakcionih šema, 20 tabela i 208 literaturnih navoda. Doktorska disertacija sadrži sledeća poglavlja: *Sažetak* (na engleskom i srpskom jeziku), *Uvod*, *Teorijski deo* (Pregled; Hemija organosiloksana – istorijat; Siloksanska veza; Sinteza polisiloksana; Sinteza polisiloksana reakcijom otvaranja prstena cikličnih siloksana; Kristalizacija polisiloksana; ²⁹Si NMR spektroskopija – moćna metoda za strukturnu analizu polisiloksana; Gel-propusna hromatografija), *Eksperimentalni deo* (Materijali; Metode karakterizacije; Priprema inicijatora α,ω -bistetrametilamonijum-oligodimetilsiloksidisilanolata (TMAS); Priprema inicijatora tetrametilamonijum-oligodimetilsiloksidisilanolata (monoTMAS); Priprema α,ω -teleheličnog dimetilvinilsiloksi oligodimetilsiloksana, terminatora krajeva lanaca (DiViEB); Reakcija otvaranja prstena cikličnih siloksana (ROP); priprema vinil-terminiranih terpolisiloksana; Priprema modelnog polimera fenil-*tris*(polidimetilsiloksana) (Ph-T-PDMS); Priprema modelnog polimera *tetrakis*(polidimetilsiloksana) (Q-PDMS); Pokušaj desililacije modelnog polimera fenil-*tris*(polidimetilsiloksana) sa monofunkcionalnim TMAS-om da bi se dobio *tetrakis*(polidimetilsiloksan); Priprema uzoraka za praćenje toka polimerizacije cikličnih siloksana inicirane silanolatom), *Rezultati i diskusija* (Pregled sintetisanih vinil-terminiranih terpolisiloksana; Polimeri koji sadrže difenilsiloksanske (DiPhS) monomerne ostatke; Polimeri koji sadrže dietilsiloksanske (DiEtS) monomerne ostatke; Praćenje toka polimerizacije otvaranjem prstena cikličnih siloksana; Polimeri koji sadrže

metilfenilsiloksanske (MePhS) monomerne ostatke), *Zaključak* i *Literatura*. Kandidat je uz tekst disertacije priložio i Biografiju i dodatke propisane pravilima Univerziteta o podnošenju doktorskih disertacija na odobravanje. Po formi i sadržaju tekst zadovoljava sve standarde Univerziteta u Beogradu za doktorsku disertaciju.

2.2. Kratak prikaz pojedinačnih poglavlja

U **Uvodu** disertacije su prikazani predmet, sadržaj, ciljevi i značaj istraživanja, koji obuhvataju razvoj novih, linearnih i potpuno amornih vinil-funkcionalizovanih terpolisiloksana. Takvi linearni kopolisiloksani našli bi primenu prvenstveno kao prekursori za pripremu niskotemperaturnih elastomera, a trenutno izazivaju veliko i naučno i praktično interesovanje u cilju dobijanja prvih elastomernih materijala za primenu u trodimenzionalnom (3D) štampanju. Predmet istraživanja obuhvatio je sintezu i karakterizaciju nekoliko serija statističkih terpolisiloksana na bazi dimetilsiloksi (DiMeS), difenilsiloksi (DiPhS), dietilsiloksi (DiEtS) ili metilfenilsiloksi (MePhS) i metilvinilsiloksi (MeViS) jedinica koje se ponavljaju, sa završnim dimetilvinilsiloksi (DiMeViS) grupama. Za sintezu kopolimera je korišćena anjonska polimerizacija otvaranjem prstena raznih smeša cikličnih siloksana, uključujući oktametilciklotetrasiloksan, D_4 , oktafenilciklotetrasiloksan, D_4^{Ph2} , oktaetilciklotetrasiloksan, D_4^{Et2} , heksaetilciklotetrasiloksan, D_3^{Et2} , tetrametiltetrafenilciklotetrasiloksan, D_4^{MePh} i tetrametiltetravinilciklotetrasiloksan, D_4^{MeVi} , u prisustvu regulatora molarne mase, teleheličnog oligodimetilsiloksana sa završnim dimetilvinil-siloksi grupama, i inicijatora, difunkcionalnog α,ω -bistetrametilamonijum-oligodimetilsiloksidisilanolata, TMAS. Reakcije polimerizacije izvođene su u rastopu. Step polimerizacije (DP) terpolisiloksana varirao je između 80 i 600, a kontrolisan je molskim odnosom regulatora molarne mase i siloksi jedinica uvedenih sa cikličnim monomerima. Difenil-, dietil- i metilfenilsiloksanski ostaci, čija je uloga suzbijanje kristalizacije polimera, ugrađivani su u polimere u sadržaju od 3 do 7 mol%. Posebna pažnja je bila posvećena rasvetljavanju mehanizma grananja lanaca u kopolimerima koji sadrže DiPhS monomerne ostatke. Značajan segment istraživanja je bio usmeren na razvoj i primenu praktičnih metoda praćenja odabranih parametara reakcije polimerizacije u navedenim sistemima, koji uključuju molarnu masu i prinos polimera, konverziju monomera, kao i mikrostrukturu polimera. Posebna pažnja je bila posvećena najkompleksnijem od svih ispitivanih sistema, kopolimerizaciji D_4 i D_4^{Ph2} , koji, pored složenosti koja potiče od istovremenog odigravanja reakcije otvaranjem prstena i reakcije ekvibracije, takođe uključuje i dodatni aspekt inicijalne heterogenosti smeše cikličnih monomera veoma različitih reaktivnosti.

Teorijski deo doktorske disertacije se sastoji od osam potpoglavlja. Prvo potpoglavlje (*Pregled*) daje veoma kratak osvrt na sadržaj Teorijskog dela. U drugom potpoglavlju (*Hemija organosiloksana – istorijska istorijat*) prikazan je redosled istraživanja u oblasti organosiloksana koja su, zahvaljujući industrijskom interesu i razvoju koji je započeo 30-tih godina dvadesetog veka, vodila do komercijalizacije i lansiranja prvih polisiloksana tokom Drugog svetskog rata. U trećem potpoglavlju (*Siloksanska veza*) detaljno je opisana elektronska konfiguracija siloksanske veze, fizička i hemijska svojstva polisiloksana koja proističu iz nje, a takođe je opisana i primena polisiloksana sa posebnim osvrtom na primenu u savremenoj tehnologiji 3Dštampanja. U četvrtom potpoglavlju (*Sinteza polisiloksana*) su navedeni postupci

za pripremu organohlorosilana, prekursora za sintezu polisiloksana, kao i načini pripreme linearnih polisiloksana polazeći od diorganodihlorosilana. U petom potpoglavlju (*Sinteza polisiloksana otvaranjem prstena cikličnih siloksana*) detaljno su opisana dosadašnja istraživanja iz oblasti anjonske i katjonske polimerizacije ciklosiloksana, pri čemu je posebna pažnja posvećena kinetičkoj i termodinamičkoj kontroli anjonskog procesa, kao i termički razgradivim baznim inicijatorima. Šesto potpoglavlje (*Kristalizacija polisiloksana*) obuhvata pregled literature koja se odnosi na kristalizaciju polisiloksana i njeno suzbijanje. Mogućnosti karakterizacije mikrostrukture i arhitekture polisiloksana koje omogućava ^{29}Si NMR spektroskopija predstavljene su u sedmom potpoglavlju (*^{29}Si NMR spektroskopija: moćna metoda za strukturnu analizu polisiloksana*). U osmom potpoglavlju (*Gel-propusna hromatografija*) je prikazan sažet pregled molekularnih parametara koje je moguće dobiti primenom ove hromatografske metode u kombinaciji sa detekcijom rasipanjem svetlosti, refraktometrijom i on-line viskozimetrom.

U **Eksperimentalnom delu** su navedeni materijali korišćeni za pripremu terpolimera, inicijatora, modelnih polimera i regulatora molarnih masa. Zatim su navedene i objašnjene metode koje su korišćene za karakterizaciju sintetisanih proizvoda. Detaljno su opisane sinteze inicijatora α,ω -bistetrametilamonijum-oligodimetilsiloksidisilanolata (TMAS) i tetrametilamonijum-oligodimetilsiloksidisilanolata (monoTMAS), terminatora krajeva lanaca i regulatora molarnih masa α,ω -teleheličnog dimetilvinilsiloksi oligodimetilsiloksana (DiViEB), vinil-terminiranih terpolisiloksana, modelnih razgranatih polimera fenil-tris(polidimetilsiloksana) (Ph-T-PDMS) i tetrakis(polidimetilsiloksana) (Q-PDMS), pokušaj desililacije modelnog polimera Ph-T-PDMS sa monofunkcionalnim TMAS-om da bi se dobio Q-PDMS, kao i priprema uzoraka za praćenje toka polimerizacije cikličnih siloksana inicirane silanolatom.

Poglavlje **Rezultati i diskusija** je organizovano u pet potpoglavlja. U prvom potpoglavlju (*Pregled sintetisanih vinil-terminiranih terpolisiloksana*) definisane su tri serije α,ω -teleheličnih, dimetilvinilsiloksi- ($\text{CH}_2=\text{CH}-\text{Si}(\text{CH}_3)_2-\text{O}-$), terminiranih terpolisiloksana, koji sadrže različite količine Me, Ph, Et and Vi bočnih grupa, sintetisanih korišćenjem anjonske polimerizacije otvaranjem prstena cikličnih siloksana, iniciranom TMAS-om. Potpoglavlje takođe sadrži rezultate karakterizacije svih terpolimera (jodometrija, SEC-MALS-VIS, viskozimetrija, NMR spektroskopija).

U okviru drugog potpoglavlja (*Polimeri koji sadrže difenilsiloksanske (DiPhS) monomernе ostatke*) opisane su dve sintetisane serije terpolisiloksana sa konstantnim ciljanim sadržajem DiPhS ostataka od 3,6 mol%. Prva serija se sastojala od 4 polimera u kojima je količinom dodatog regulatora molarne mase (DiViEB) variran ciljani stepen polimerizacije (DP) od 80 do 600, dok je molski odnos DiViEB i TMAS ($[\text{DiViEB}]/[\text{TMAS}]$) održavan na konstantnom nivou od 2/1. U drugoj seriji od 6 polimera $[\text{DiViEB}]/[\text{TMAS}]$ odnos je menjan u širokom opsegu od 20/1 do 1/1, pri čemu je ciljani DP bio konstantan (DP=160). DSC merenja su pokazala da je dodatkom 3,6 mol% DiPhS jedinica kompletno sprečena kristalizacija PDMS-a. Zahvaljujući podacima dobijenim ^{29}Si NMR i SEC-MALS-VISC analizama ustanovljeno je da se u ovim polimerima odvija grananje lanaca. Na osnovu činjenice da je u ^{29}Si NMR spektrima izučavanih polisiloksana prisutan signal na -80 ppm, poreklom od fenil trisiloksi- silicijuma (Ph-T), čiji relativni intenzitet (u odnosu na intenzitet signala poreklom od DiPhS monomernih jedinica) raste sa koncentracijom TMAS inicijatora, predložen je mehanizam grananja u

polimerima koji sadrže DiPhS monomerne jedinice. Predloženi mehanizam grananja obuhvata nukleofilni napad silanolatom na polarne bočne Si-C_{Ar} veze iz DiPhS jedinica i sledstvenu zamenu fenil grupa polisiloksanskim lancima, koje rezultira formiranjem Ph-T i Q monomernih jedinica (tačkaka grananja). ²⁹Si NMR karakterizacijom sintetisanih modelnih razgranatih polimera fenil-*tris*(polidimetilsiloksana) (Ph-T-PDMS) i *tetrakis*(polidimetilsiloksana) (Q-PDMS) potvrđeni su ispravnost pretpostavke o formiranju Ph-T tačkaka grananja (²⁹Si NMR signal na -80 ppm) i odsustvo kvaternernih, Q, tačkaka grananja, redom, u polimerima koji sadrže DiPhS monomerne ostatke. Pokušaj desililacije Si-C_{Ar} veze modelnog razgranatog polimera (Ph-T-PDMS) nije vodio formiranju Q struktura, čime je eksperimentalno dokazano da mehanizam grananja u ispitivanim terpolisiloksanima ne podrazumeva totalnu desililaciju DiPhS grupe. SEC-MALS-VISC analize su pokazale da su molarne mase po brojnoj zastupljenosti sintetisanih terpolisiloksana, usled odigravanja sporednih reakcija desililacije koje vode grananju lanaca, znatno više od ciljanih, kao i da njihova polidisperznost značajno raste sa koncentracijom korišćenog inicijatora. SEC-MALS-VISC merenja su takođe omogućila određivanje vrednosti eksponenta *a* iz Mark-Houwink-Sakurada (MHS) jednačine ($[\eta]=KM^a$) koji sadrži informaciju o konformaciji polimernih lanaca. Vrednosti MHS eksponenta *a* za većinu terpolisiloksana koji sadrže DiPhS monomerne jedinice su manje od 0,5, ukazujući na naglašenu kompaktnost makromolekula tipičnu za razgranate polimere.

U trećem potpoglavlju (*Polimeri koji sadrže dietilsiloksanske (DiEtS) monomerne ostatke*) je opisan razvoj novih terpolisiloksana u kojima su difenilsiloksanske monomerne jedinice zamenjene dietilsiloksanskim. Polazna hipoteza je bila da bi zamena bočnih fenil grupa u kopolimerima voluminoznim etil grupama podjednako dobro suzbila njihovu kristalizaciju, istovremeno sprečavajući grananje lanaca smanjenjem elektrofilnosti fenil supstituisanog silicijuma i sledstvenim smanjivanjem njegove podložnosti nukleofilnom napadu aktivnih silanolatnih centara. Tri serije polisiloksana su pripremljene koristeći različite izvore DiEtS jedinica: a) heksaetilciklotrisiloksan, D₃^{Et2}, b) oktaetilciklotetrasiloksan, D₄^{Et2} i c) DiEtS hidrolizat, koji predstavlja komercijalnu smešu cikličnih siloksana i linearnog polidietilsiloksana, PDES, srednje molarne mase (17000). Dok su svi polimeri pripremljeni sa čistim D₃^{Et2} i D₄^{Et2} pokazali odsustvo kristaliničnosti, pokušaj suzbijanja kristalizacije PDMS-a korišćenjem DiEtS-hidrolizata nije uspeo. ²⁹Si NMR analizom hidrolizata je ustanovljeno prisustvo dužih PDES blokova (signal na -23 ppm) poreklom iz linearne frakcije DiEtS-hidrolizata, koja nije efektivno učestvovala u reakcijama ekvibracije. SEC-MALS-VISC analizom je potvrđena kompletna linearnost svih polimera koji sadrže DiEtS monomerne ostatke: molarne mase u ciljanom opsegu, polidisperznost od 1,5 do 2, tipična za kompletno ekvilibrisane linearne polisiloksane i konformacija u razblaženim rastvorima karakteristična za linearne polimere u termodinamički dobrom rastvaraču.

U četvrtom potpoglavlju (*Praćenje toka polimerizacije otvaranjem prstena cikličnih siloksana*) je razmatrana dinamika polimerizacije ciklosiloksana u terpolisiloksan sistemima koji sadrže DiPhS i DiEtS monomerne jedinice, kao i u referentnom sistemu, PDMS homopolimeru. Odvijanje reakcija je praćeno korišćenjem SEC, TGA i ²⁹Si NMR metoda. Dok su se homopolimerizacija D₄ i kopolimerizacija D₄ sa D₃^{Et2} odvijale na približno identičan način, sa karakterističnim brzim rastom polimera i njegovog prinosa, kopolimerizaciju D₄ sa D₄^{Ph2} je pratio izražen indukcion period kao posledica umanjene rastvorljivosti D₄^{Ph2} u D₄ i znatno veće reaktivnosti D₄^{Ph2} od D₄ ka dimetilsilanolatu. Predložen je novi mehanizam

kopolimerizacije D₄ i D₄^{Ph₂} koji obuhvata a) inicijalno formiranje kratkih linearnih B-A-B triblokova koji se sastoje od DiMeS (A) segmenata poreklom od TMAH inicijatora i DiPhS (B) segmenata, b) formiranje A-B-A-B-A pentablokova i c) redistribuciju multiblokova reakcijom ekvibracije siloksana, rezultirajući formiranjem polimera u kome alterniraju izolovane DiPhS monomerne jedinice i PDMS segmenti.

Kako je analizom grananja lanaca u terpolisiloksanima koji sadrže DiPhS monomerne jedinice demonstrirano i u eksperimentima sa modelnim razgranatim PDMS-om potvrđeno, totalna desililacija DiPhS grupe koja bi vodila formiranju Q tačaka grananja se *ne* odvija usled dramatično umanjene elektrofilitnosti silicijuma iz fenil-T monomerne jedinice i stoga umanjene podložnosti ka nukleofilnom napadu silanolata. Na bazi tih rezultata, u petom potpoglavlju (*Polimeri koji sadrže metilfenilsiloksanske (MePhS) monomerne ostatke*) je postulirano da bi terpolisiloksani koji sadrže metilfenilsiloksanske (MePhS) monomerne jedinice bili potpuno otporni na nukleofilne napade silanolata, zadržavajući perfektno linearnu konfiguraciju lanaca uz istovremeno suzbijanje kristalizacije. Karakterizacijom sintetisanih terpolisiloksana sa MePhS monomernim jedinicama (²⁹Si NMR, SEC-MALS-VISC) potvrđeno je da su isti, pored potpune amorfnosti, takođe zadržali linearnost lanaca, čime je dokazana ispravnost navedenih postulata. Ogledi u kojima je praćen tok reakcije kopolimerizacije pokazali su da su za sistem koji sadrži MePhS monomerne jedinice, slično homopolimerizaciji D₄ i kopolimerizaciji D₄ i D₃^{Et₂}, svojstveni brz rast polimera i prinosa, kao i izuzetno efikasna nasumična raspodela MePhS jedinica duž lanaca polimera.

U poglavlju **Zaključak** su sumirani najvažniji zaključci izvedeni na osnovu ispitivanja izloženih u prethodnim poglavljima.

Poglavlje **Literatura** sadrži literaturne navode citirane u disertaciji, kao i radove proistekle iz istraživanja u okviru disertacije.

3. OCENA DISERTACIJE

3.1. Savremenost i originalnost

Polisiloksani, zbog neobične kombinacije svojstava, koja uključuju fleksibilnost u širokom rasponu temperatura, izuzetnu termičku i termoksidativnu stabilnost, jedinstvena površinska svojstva, optičku transparentnost, visoku propustljivost za gasove, biokompatibilnost, itd., tradicionalno nalaze široku primenu u brojnim oblastima. Poslednjih godina primena polisiloksanskih elastomera u 3D štampi, koja je definisana kao tehnologija precizne izrade trodimenzionalnih objekata delikatnih geometrija propisane mikroarhitekture iz digitalne datoteke, je privukla veliku pažnju akademske i industrijske javnosti. Ovi postupci nanošenja sloj po sloj umreženog polimernog materijala nedvosmisleno omogućavaju postizanje novih funkcionalnosti ili poboljšane performanse materijala, koje je nemoguće postići tradicionalnim postupcima prerade elastomera. Uporedo sa brzim napredovanjem tehnologije 3D štampanja progresivno raste industrijska potražnja za dobro definisanim funkcionalnim polisiloksanima koji bi omogućili preciznu izradu kompleksnih oblika, kako bi se proširila njihova primena.

Inherentna fleksibilnost lanaca polisiloksana, koja je posledica neuobičajeno duge siloksanske veze, širokog Si-O-Si ugla kao i veoma slabih interakcija među segmentima, potencijalno ih čini savršenim kandidatima za prekursore za niskotemperaturne elastomere.

Glavni nedostatak za ovakvu primenu polisiloksana, uprkos izuzetnoj elastičnosti na ekstremno niskim temperaturama, predstavlja njihova naglašena tendencija ka kristalizaciji, kojom se značajno sužava temperaturni opseg upotrebljivosti njihovih elastomera. U slučaju polidimetilsiloksana, PDMS, komercijalno najzastupljenijeg predstavnika ove grupe polimera, kompletno suzbijanje kristalizacije se veoma lako postiže supstitucijom malih količina bočnih metil grupa velikim i glomaznim fenilnim grupama. Drugi kritičan aspekt za uspešnu primenu siloksanskih elastomera predstavlja dobro definisana, regularna struktura mreža. Stoga je neophodno da se sintetske strategije za pripremu prekursora za siloksanske mreže fokusiraju na postizanju linearnosti prekursora kao i njihove uniformne funkcionalizacije. Nelinearnost prekursora usled grananja lanaca bi vodila formiranju nesavršenosti mreža, kao što su elastično neaktivni viseći lanci. Zbog toga je, da bi se obezbedila predvidljiva gumolika elastičnost siloksanskog elastomera na ekstremno niskim temperaturama, neophodno eliminisati mogućnost grananja lanaca uz istovremeno suzbijanje kristalizacije polimera.

U skladu sa prethodno navedenim, istraživanja sprovedena u okviru ove doktorske disertacije bila su fokusirana na izučavanje uticaja strukture različitih cikličnih siloksana na linearnost i termičke prelaze njihovih polimera sa ciljem da se razviju dobro definisani prekursori namenjeni za pripremu niskotemperaturnih elastomera. Iz tog razloga je, reakcijom anjonske polimerizacije otvaranjem prstena, sintetisano nekoliko serija statističkih, vinil funkcionalizovanih kopolisiloksana, koji su duž svojih lanaca osim dominantnih, dimetilsiloksanskih, DiMeS, sadržali statistički raspoređene male količine (3-7 mol%) difenilsiloksanskih, DiPhS, dietilsiloksanskih, DiEtS, ili metilfenilsiloksanskih, MePhS, monomernih jedinica. Dok je inkorporacijom svih navedenih glomaznih komonomera uspešno suzbijena kristalizacija PDMS-a, čime je obezbeđena kompletna amorfnost materijala, ustanovljeno je da polimeri koji sadrže DiPhS jedinice u prisustvu nukleofilnog inicijatora (silanolata) podležu reakciji desililacije Si-C_{Ar} bočnih veza, što rezultuje grananjem lanaca. Takođe je dokazano da mehanizam grananja lanaca u ovim polimerima ne podrazumeva potpunu desililaciju, usled toga što supstitucija prve Ph grupe u DiPhS segmentu polisiloksanskim lancem značajno umanjuje elektrofilnost silicijuma, te tim i njegovu podložnost sledećem nukleofilnom napadu.

Značajan segment istraživanja bio je usmeren na razvoj i primenu praktičnih metoda praćenja odabranih parametara reakcije polimerizacije, koji uključuju molarnu masu i prinos polimera, konverziju monomera, kao i mikrostrukturu polimera u navedenim sistemima. Posebna pažnja bila je usmerena na najkompleksniji sistem, kopolimerizaciju D₄ i D₄^{Ph²} monomera, koja uključuje karakterističan indukcion period, usled veoma niskog stepena mešljivosti i značajne razlike u reaktivnosti ovih monomera prema silanolatu. Na osnovu hromatografskih, spektroskopskih rezultata i rezultata termičke degradacije, dobijenih iz ovih eksperimenata, predložen je novi trostepeni reakcioni mehanizam kojim je detaljno opisana dinamika kopolimerizacije u ovom kompleksnom sistemu. Nasuprot procesima sa monomerima D₄ i D₄^{Ph²}, oni u sistemima pripremanim sa D₃^{Et²} i D₄^{MePh} komonomerima, odlikovali su se veoma brzim rastom molarnih masa i prinosa polimera, kao i veoma efikasnom redistribucijom ostataka monomera. Činjenica da je ovako efikasnom pripremom kompletno amorfni terpolisiloksana koji sadrže DiEtS ili MePhS monomerne jedinice takođe potpuno eliminisana mogućnost grananja njihovih lanaca čini ih idealnim kandidatima za prekursore niskotemperaturnih elastomera.

3.2. Osvrt na referentnu i korišćenu literaturu

Doktorska disertacija sadrži 208 literaturnih navoda, koji su vezani za istraživanja od značaja za problematiku obrađenu u disertaciji. Pregledana literatura se odnosi na a) hemiju siloksana sa posebnim osvrtom na polimerizaciju otvaranjem prstena cikličnih monomera i kinetičku i termodinamičku kontrolu procesa, b) fenomen kristalizacije polisiloksana i sintetske postupke kojima se kristalizacija suzbija i c) savremene metode karakterizacije polisiloksana. Kroz obradu aktuelne literature u svim delovima disertacije, kandidat je dao izvanrednu sintezu poznatog znanja iz oblasti sinteze, karakterizacije i primene polisiloksana. Iz spiska literaturnih navoda može se zaključiti da kandidat prati i dobro razume aktuelne trendove u oblastima istraživanja koje obuhvata ova doktorska disertacija.

3.3. Opis i adekvatnost primenjenih naučnih metoda

Istraživanja sprovedena u okviru ove doktorske disertacije podrazumevala su primenu odgovarajućih originalnih ili modifikovanih metoda za sintezu terpolisiloksana, inicijatora, regulatora molarnih masa i modelnih razgranatih oligomera, kao i savremenih eksperimentalnih tehnika za karakterizaciju, kojima su potvrđivane polazne pretpostavke.

Za pripremu terpolisiloksana primenjen je postupak anjonske polimerizacije otvaranjem prstena cikličnih monomera inicirane tetrametilamonijum silanolatom (TMAS). Regulator molarnih masa i modelni razgranati polimeri sintetisani su niskotemperaturnom katjonskom polimerizacijom u prisustvu jonoizmenjivačke smole Amberlyst 15. Inicijator tetrametilamonijumsilanolat (TMAS) sintetisan je reakcijom tetrametilamonijum hidroksida pentahidrata $((\text{CH}_3)_4\text{NOH}\cdot 5\text{H}_2\text{O})$ i D_4 pri kojoj je reakcijom generisana i kristalna voda uklanjana azeotropskom destilacijom u prisustvu cikloheksana.

Molarne mase, raspodela molarnih masa, veličina i konformacija sintetisanih polimera su određivane upotrebom gel-propusne hromatografije kuplovane sa detektorom rasipanja svetlosti pod raznim uglovima, on-line viskozimetrom i diferencijalnim refraktometrom (SEC/MALS/VIS/RI). Konverzija monomera tokom polimerizacije određivana je na osnovu rezultata gel-propusne hromatografije sa detektorom indeksa refrakcije. Sastav i mikrostruktura sintetisanih polimera i inicijatora proučavani su pomoću nuklearne-magnetne rezonance (^1H NMR, ^{29}Si NMR). Temperature topljenja i kristalizacije sintetisanih polimera određivane su pomoću diferencijalne skenirajuće kalorimetrije (DSC). Relativni udeo ciklične i linearne komponente (prinos polimera) određivan je termogravimetrijskom analizom (TGA) uzoraka reakcione smeše uzimanih u različitim vremenskim intervalima tokom odigravanja reakcije. Dinamička viskoznost izolovanih uzoraka polimera merena je uz pomoć reometra sa geometrijom konusa i ploče. Sadržaj vinilnih grupa u pripremljenim polimerima i oligomerima određivan je jodometrijskom titracijom.

3.4. Primenljivost ostvarenih rezultata

Budući da je primena siloksanskih elastomera u tehnologiji 3D štampanja u žiži interesovanja akademske i industrijske javnosti, rezultati istraživanja realizovanih u okviru ove doktorske disertacije dali su značajan doprinos u pravcu razvoja dobro definisanih, linearnih

polisiloksanskih prekursora koji zadržavaju elastičnost na ekstremno niskim temperaturama. Naročito su bitna fundamentalna saznanja do kojih se došlo tokom ovih istraživanja, koja se odnose na nove predložene mehanizme grananja i kopolimerizacije u kompleksnim sistemima koji uključuju DiPhS monomerne jedinice. Nova saznanja su, zahvaljujući boljem razumevanju strukture i svojstava razmatranih kopolimera, omogućila razvoj nekoliko vrsta terpolisiloksana različitog sastava, kojim je garantovana priprema prekursora zahtevanog kvaliteta. Naučna verifikacija rezultata ove doktorske disertacije potvrđena je u radovima objavljenim u međunarodnim časopisima izuzetnih vrednosti.

3.5. Ocena dostignutih sposobnosti kandidata za samostalni naučni rad

Tokom izrade ove doktorske disertacije kandidat Alisa Zlatanić, magistar tehničkih nauka, je pokazala stručnost i samostalnost u pretraživanju i korišćenju naučne literature, planiranju, dizajnu i realizaciji eksperimenata, obradi i interpretaciji dobijenih podataka, diskusiji rezultata i pripremi publikacija. Takođe, nadogradila je postojeću bazu znanja iz oblasti sinteze i karakterizacije polimera ovladavanjem raznim postupcima za sintezu polisiloksana, kao i savremenim eksperimentalnim tehnikama karakterizacije polimera. Komisija je na osnovu dosadašnjeg zalaganja i postignutih rezultata, kao i na osnovu sadržaja podnete doktorske disertacije, utvrdila da kandidat poseduje sve kvalitete neophodne za samostalni naučno-istraživački rad.

4. OSTVARENI NAUČNI DOPRINOS

4.1. Prikaz ostvarenih naučnih doprinosa

Kandidat Alisa Zlatanić je u okviru ove doktorske disertacije ostvarila značajan doprinos u razvoju i ispitivanju novih vinil-funkcionalnih polisiloksana, prekursora za elastomere sa poboljšanom strukturom, termičkim i mehaničkim svojstvima. Naučni doprinosi rezultata istraživanja ostvarenih tokom izrade ove doktorske disertacije obuhvataju:

- Određivanje detaljnog mehanizma reakcije grananja lanaca terpolisiloksana koji sadrže DiPhS monomerne ostatke tokom anjonske polimerizacije cikličnih siloksana u prisustvu TMAS inicijatora;
- Kvantifikaciju stepena grananja u terpolisiloksanima raznih stepena polimerizacije koji sadrže DiPhS monomerne ostatke;
- Određivanje kritičnih koncentracija silanolata pri kojima dolazi do grananja prilikom sinteze terpolisiloksana koji sadrže DiPhS monomerne ostatke;
- Poređenje efikasnosti supstitucije metil grupa etil grupama upotrebom tri tipa dietilsiloksanskih monomera: D_3^{Et2} , D_4^{Et2} i DiEt hidrolizata;
- Utvrđivanje mogućnosti i efikasnosti sprečavanja kristalizacije i grananja polisiloksana zamenom DiPhS jedinica koje se ponavljaju DiEtS i MePhS analogima;
- Određivanje minimalnog stepena inkorporacije DiEtS ili MePhS segmenata u linearnim terpolisiloksanima koji vodi kompletnom suzbijanju kristalizacije;

- Utvrđivanje mehanizma anjonske kopolimerizacije difenil i dimetil supstituisanih cikličnih oligosiloksanskih monomera.

4.2. Kritička analiza rezultata istraživanja

Istraživanja prikazana u ovoj doktorskoj disertaciji su, nakon detaljne analize stanja istraživanja u razmatranoj oblasti, koncipirana sa dva osnovna cilja: a) razvoj novih, potpuno amorfnih i isključivo linearnih polisiloksana, pogodnih za primenu na ekstremnim temperaturama, i b) detaljna analiza procesa dobijanja ovakvih polimera reakcijom anjonske polimerizacije otvaranjem prstena odabranih ciklosiloksana u rastopu. Svojstva i performanse umreženih elastomera primarno zavise od strukture i arhitekture polisiloksanskih prekursora korišćenih za njihovu pripremu. Da bi se sačuvala gumolika elastičnost siloksanskih elastomera na ekstremno niskim temperaturama i time postigao širok temperaturni interval upotrebljivosti, neophodna je potpuna eliminacija kristaliničnosti u njihovim polisiloksanskim prekursorima. Takođe je neophodno obezbediti linearnost lanaca polisiloksana kako bi se sprečilo, ili svelo na najmanju meru, prisustvo neidealnosti mreže u formi elastično neaktivnih visećih lanaca, koji narušavaju regularnost umrežene strukture i time mehanička svojstva elastomera. U skladu sa navedenim ciljevima, u ovoj doktorskoj disertaciji je a) detaljno rasvetljen mehanizam grananja kojem su podložni difenil supstituisani polisiloksani tokom anjonske polimerizacije ciklosiloksana, b) određene kritične koncentracije silanolata pri kojima započinje grananje prilikom sinteze difenil supstituisanih polisiloksana, c) dokazana mogućnost i efikasnost suzbijanja kristalizacije i grananja polisiloksana dobijenih zamenom DiPhS jedinica DiEtS i MePhS analogima, i d) predložen mehanizam anjonske kopolimerizacije difenil i dimetil supstituisanih cikličnih siloksana kojim je objašnjen usporen početak razmatrane reakcije.

Upoređivanjem postavljenih ciljeva rada sa postignutim rezultatima, Komisija je konstatovala da ostvarena istraživanja u potpunosti zadovoljavaju kriterijume doktorske disertacije. Na osnovu savremenih metoda istraživanja i analize primenjenih u ovoj disertaciji, zaključeno je da su ostvareni rezultati od izuzetnog značaja ne samo sa naučnog već i sa praktičnog aspekta.

4.3. Verifikacija naučnih doprinosa

Kandidat Alisa Zlatanić je ostvarila značajne rezultate u oblasti istraživanja na koju se odnosi ova doktorska disertacija, a koji su verifikovani objavljenim radovima u časopisima međunarodnog značaja i saopštenim na naučnim skupovima. Iz doktorske disertacije su publikovana dva naučna rada u međunarodnom časopisu izuzetnih vrednosti (M21a) i jedan rad u vrhunskom međunarodnom časopisu (M21). Deo rezultata istraživanja je saopšten na naučnim skupovima nacionalnog značaja (M64).

Kategorija M21a (Radovi u međunarodnom časopisu izuzetnih vrednosti)

1. **Zlatanic, A.**, Radojčić, D., Wan, X., Messman, J. M., Dvornic, P. R., *Monitoring of the Course of the Silanolate-Initiated Polymerization of Cyclic Siloxanes. A Mechanism for the Copolymerization of Dimethyl and Diphenyl Monomers*. *Macromolecules* 51, 895-905 (2018) (ISSN: 0024-9297, IF(2017): 5,914)

2. **Zlatanic A.**, Radojic D., Wan X., Messman J. M., Dvornic P. R., *Suppression of Crystallization in Polydimethylsiloxanes and Chain Branching in Their Phenyl-Containing Copolymers*. *Macromolecules*, 50, 3532-3543 (2017) (ISSN: 0024-9297, IF(2016): 5,835)

Kategorija M21 (Rad u vrhunskom međunarodnom časopisu)

1. **Zlatanic A.**, Radojic D., Wan X., Messman J. M., Bowen D. E., Dvornic P. R., *Dimethyl-Methylphenyl Copolysiloxanes by Dimethylsilanolate-Initiated Ring Opening Polymerization. Evidence for Linearity of the Resulting Polymer Structures*, *Journal of Polymer Science Part A: Polymer Chemistry*, doi: 10.1002/pola.29367 (2019), (ISSN: 0887-624X, IF(2017):2,588)

Kategorija M64 (Radovi saopšteni na skupovima nacionalnog značaja)

1. **Zlatanic A.**, Radojic D., Wan X., Messman M. J., Dvornic R.P., *Synthesis and Characterization of Polysiloxane Terpolymers Containing Methyl, Ethyl, Phenyl and Vinyl Siloxy Units*, 43rd Polymeric Materials, Adhesives, and Composites Conference (PolyMAC), Kansas City, MO, June 14–16, 2016.
2. Radojic D., **Zlatanic A.**, Wan X., Messman M. J., Dvornic R. P., *Quantitative Analysis of Microstructure in Dimethylvinyl Terminated Dimethyl, Diphenyl, MethylVinyl Containing Siloxane Copolymers by ²⁹Si NMR*, 51st Midwest Regional ACS Meeting, Manhattan, KS, October 26-28, 2016.
3. Wan X., **Zlatanic A.**, Messman M. J., Dvornic R.P., *Characterization of Molecular Weights and Structures of Polysiloxanes by SEC with Triple Detection Capability*, Pentasectional Regional ACS Meeting, Bartlesville, OK, April 8-9, 2016.
4. **Zlatanic A.**, Radojic D., Wan M., Bergman E. J., Messman M.J., Bowen E.D., Dvornic R.P., *Synthesis and Characterization of Silicone Gum Precursors*, Silicone Summit, Kansas City, MO, November 10-12, 2015.

Kandidat je i koautor jednog rada objavljenog u vrhunskom međunarodnom časopisu (M21) koji se odnosi na primenu terpolisiloksana razvijenih tokom izrade ove doktorske disertacije u tehnologiji 3D štampanja.

Kategorija M21 (Rad u vrhunskom međunarodnom časopisu)

1. Serrine, J. M.; **Zlatanic, A.**; Meenakshisundaram, V.; Messman, J. M.; Williams, C. B.; Dvornic, P. R.; Long, T. E. 3D Printing Amorphous Polysiloxane Terpolymers via Vat Photopolymerization. *Macromolecular Chemistry and Physics* 220, 1800425 (2019) (ISSN: 1521-3935, IF(2018): 2.492)

5. ZAKLJUČAK I PREDLOG

Na osnovu svega napred iznetog Komisija smatra da doktorska disertacija Alise Zlatanić predstavlja originalan naučni doprinos u oblasti sinteze i karakterizacije polisiloksana. Novi, potpuno amorfni i linearni vinil-funkcionalni terpolimeri pripremani anjonskom polimerizacijom ciklosiloksana su u potpunosti okarakterisani u pogledu mikrostrukture, veličine i raspodele molarnih masa, termičkih i reoloških svojstava, kao i sadržaja vinilnih

funkcionalnih grupa. Rasvetljavanjem mehanizama grananja lanaca i reakcije kopolimerizacije u difenil supstituisanim sistemima ostvaren je dragocen doprinos u izučavanju uticaja strukture monomera na svojstva polisiloksana i tok reakcije polimerizacije. Imajući u vidu kvalitet, obim i naučni doprinos postignutih rezultata, Komisija predlaže Nastavno-naučnom veću Tehnološko-metalurškog fakulteta Univerziteta u Beogradu da prihvati ovaj Referat i da ga zajedno sa podnetom disertacijom Alise Zlatanić, magistra tehničkih nauka, pod nazivom „Uticaj strukture cikličnih monomera na tok anjonske polimerizacije i svojstva vinyl-terminiranih polisiloksana (The Effect of Structure of Cyclic Monomers on the Course of Anionic Polymerization and Properties of Vinyl-Terminated Polysiloxanes)“, izloži na uvid javnosti i nakon isteka zakonom predviđenog roka, uputi na konačno usvajanje Veću naučnih oblasti prirodnih nauka Univerziteta u Beogradu, te nakon završetka ove procedure, pozove kandidata na usmenu odbranu doktorske disertacije pred Komisijom u istom sastavu.

U Beogradu, 15.04.2019. godine

ČLANOVI KOMISIJE

Dr Ivanka Popović, redovni profesor

Univerziteta u Beogradu, Tehnološko-metalurški fakultet

Dr Petar R. Dvornić, redovni profesor

Državni univerzitet u Pittsburgu, Fakultet umetnosti i nauka

Dr Jasna Đonlagić, redovni profesor u penziji

Univerziteta u Beogradu, Tehnološko-metalurški fakultet

Dr Melina Kalagasidis Krušić, redovni profesor

Univerziteta u Beogradu, Tehnološko-metalurški fakultet

Dr Aleksandar Popović, redovni profesor

Univerziteta u Beogradu, Hemijski fakultet

**UNIVERSITY OF BELGRADE
FACULTY OF TECHNOLOGY AND METALLURGY
TO THE SCIENTIFIC AND ACADEMIC COUNCIL**

Subject: Report on the assessment of completed doctoral dissertation of candidate Alisa Zlatanić

By the decision of the Scientific and Academic Council of the Faculty of Technology and Metallurgy of the University of Belgrade No.35/77 from 07.03.2019. we are appointed to the Committee for the assessment of completed doctoral dissertation of candidate Alisa Zlatanić, M.Sci., entitled

„The Effect of Structure of Cyclic Monomers on the Course of Anionic Polymerization and Properties of Vinyl-Terminated Polysiloxanes“

„Uticaj strukture cikličnih monomera na tok anjonske polimerizacije i svojstva vinil-terminiranih polisiloksana“

Upon examining the submitted dissertation and other supporting materials and interviewing the candidate, the Committee submits the following

R E P O R T

1. INTRODUCTION

1.1. Chronology of approval of the dissertation

- In the academic year 2016/2017, the candidate Alisa Zlatanić, M.Sci., enrolled in the third year of doctoral academic studies at the Faculty of Technology and Metallurgy, University of Belgrade, profile Chemistry.
- 15.03.2018. – The candidate Alisa Zlatanić proposed the topic for doctoral dissertation to be completed at the Faculty of Technology and Metallurgy, Belgrade University, entitled „The Effect of Structure of Cyclic Monomers on the Course of Anionic Polymerization and Properties of Vinyl-Terminated Polysiloxanes (Uticaj strukture cikličnih monomera na tok anjonske polimerizacije i svojstva vinil-terminiranih polisiloksana)“.
- 29.03.2018. - At the session of the Scientific and Academic Council of the Faculty of Technology and Metallurgy, University of Belgrade, the decision was made (No. 35/92) to members of the Committee for the assessment of eligibility of the candidate Alisa Zlatanić,

M.Sci., and scientific validity of the proposed topic of doctoral dissertation entitled „The Effect of Structure of Cyclic Monomers on the Course of Anionic Polymerization and Properties of Vinyl-Terminated Polysiloxanes (Uticaj strukture cikličnih monomera na tok anjonske polimerizacije i svojstva vinil-terminiranih polisiloksana)“.

- 26.04.2018. - At the session of the Scientific and Academic Council of the Faculty of Technology and Metallurgy, University of Belgrade, the decision was made (No. 35/161) to accept the Report prepared by the Committee for the assessment of eligibility of the candidate Alisa Zlatanić and scientific validity of the proposed topic for completion of doctoral dissertation entitled „The Effect of Structure of Cyclic Monomers on the Course of Anionic Polymerization and Properties of Vinyl-Terminated Polysiloxanes (Uticaj strukture cikličnih monomera na tok anjonske polimerizacije i svojstva vinil-terminiranih polisiloksana)“. Dr. Marija Nikolić, associate professor of the Faculty of Technology and Metallurgy, University of Belgrade was appointed as mentor.
- 28.06.2018. - At the session of the Professional Board for Natural Sciences of the University of Belgrade, the approval was given (number 61206-2265/4-18) for the proposed topic of doctoral dissertation of the candidate Alisa Zlatanić, M.Sci., entitled „The Effect of Structure of Cyclic Monomers on the Course of Anionic Polymerization and Properties of Vinyl-Terminated Polysiloxanes (Uticaj strukture cikličnih monomera na tok anjonske polimerizacije i svojstva vinil-terminiranih polisiloksana)“.
- 07.03.2019. - At the session of the Scientific and Academic Council of the Faculty of Technology and Metallurgy, University of Belgrade, by decision No. 35/77, the Committee was appointed for the assessment of completed doctoral dissertation of the candidate Alisa Zlatanić, M.Sci., entitled „The Effect of Structure of Cyclic Monomers on the Course of Anionic Polymerization and Properties of Vinyl-Terminated Polysiloxanes (Uticaj strukture cikličnih monomera na tok anjonske polimerizacije i svojstva vinil-terminiranih polisiloksana)“. Dr. Ivanka Popovic, full professor at the Faculty of Technology and Metallurgy, University of Belgrade, was elected the President of the Committee.

1.2. The scientific field of the dissertation

Research in this doctoral dissertation belongs to the scientific field of Science of Chemistry, subfield Chemistry, for which the Faculty of Technology and Metallurgy, University of Belgrade is the accredited institution. The mentor is Dr. Marija Nikolić, associate professor at the Faculty of Technology and Metallurgy, who is, based on previous publishing and research experience, fully competent to lead the preparation of this doctoral dissertation.

1.3. Biography of the candidate

Alisa Zlatanić was born on 08.04.1967. in Pljevlja. She attended elementary and high school in Priboj. She enrolled in undergraduate studies at the Faculty of Technology and Metallurgy of the

University of Belgrade in the academic year 1985/86. She graduated on 15.02.1993. within the study program Organic Chemical Technology and Polymer Engineering defending the thesis entitled: „Synthesis and Characterization of Unsaturated Polyesters with Terminal Acrylate Groups”. Afterwards, she attended postgraduate studies from the academic year 1994/95, in the field of Chemistry and Engineering of Polymers. Passing all the exams foreseen by the curriculum for the master's program with an average grade of 9.89, she finished her master's degree on 10.20.1997., defending the master thesis entitled: „Synthesis and Rheological Behavior of Unsaturated Polyesters with Terminal Acrylate Groups”. Alisa Zlatanić enrolled in the third year of doctoral studies at the Faculty of Technology and Metallurgy of the University of Belgrade in the academic year 2016/17, study program Chemistry.

Alisa Zlatanić, M.Sci., was employed at the Department for General and Inorganic Chemistry of the Faculty of Technology and Metallurgy of the University of Belgrade from 06.12.1993. to 31.10.1999., first as a Teaching and Research Assistant then as a Teaching and Research Associate (promoted Associate on 12.10.1998). Since 01.11.1999., she has been employed as Senior Research Associate at Kansas Polymer Research Center (KPRC) of Pittsburg State University (PSU), in Pittsburg, Kansas, US.

The field of scientific and research work of Alisa Zlatanić includes the synthesis, characterization and application of polymers, such as polysiloxanes, polyesters, polyethers, polyurethanes, polyacrylamides. Significant part of that work was dedicated to studying the polymers based on natural and model triglycerides and their application and commercialization in the technical area of cellular polyurethane materials, adhesives and composites. Beginning in early 2015, Alisa Zlatanić has been, under the guidance of Professor Petar Dvornić, actively engaged in the collaborative project between Pittsburg State University and Honeywell FM&T, focused on the research and development of polysiloxane elastomers, closely related to the topic of her doctoral dissertation.

As a result of her entire scientific research, Alisa Zlatanić has published a chapter in an international monograph (M14), 15 full papers in international scientific journals (3 M21a, 7 M21, 3 M22, 2 M23), more than 30 proceedings from national and international conferences, two patents and one patent application.

Alisa Zlatanić is the recipient of the "Presidential Green Chemistry Challenge Award" for 2007 in the category of Design for Cleaner Chemicals, by which the US Environmental Protection Agency (EPA) awarded a team of researchers of Kansas Polymer Research Center of Pittsburg State University and the company Cargill Inc. for fruitful cooperation during the development and commercialization of BiOHTM line of polyols based on natural oils.

Alisa Zlatanić has been a member of the American Chemical Society since 2002.

2. DESCRIPTION OF DISSERTATION

2.1. The content of the dissertation

The doctoral dissertation of the candidate Alisa Zlatanić was written in English and contains 142 pages (A4), 58 figures, 16 reaction schemes, 20 tables and 208 literature citations. It consists of the following chapters: *Abstract* (in English and Serbian), *Introduction*, *Theoretical Part* (Overview, Chemistry of Organosiloxanes - Historical Background, The Siloxane Bond, Synthesis of Polysiloxanes, Synthesis of Polysiloxanes via Ring Opening Polymerization of Cyclic Siloxanes, Crystallization of Polysiloxanes, ^{29}Si NMR Spectroscopy: A Powerful Tool for Structural Analysis of Polysiloxanes, Size Exclusion Chromatography), *Experimental* (Materials, Characterization Methods, Preparation of α,ω -bisTetramethylammonium-Oligodimethylsiloxysilanolate Initiator (TMAS), Preparation of Tetramethylammonium-Oligodimethylsiloxysilanolate Initiator (monoTMAS), Preparation of α,ω -Telechelic Dimethylvinylsiloxy End-Blocker (DiViEB), Ring Opening Polymerization of Cyclic Siloxanes (ROP): Preparation of Vinyl-Terminated Terpolysiloxanes, Preparation of Model Phenyl-tris(Polydimethylsiloxane) (Ph-T-PDMS) 3-Armed Star Polymer, Preparation of Model tetrakis(Polydimethylsiloxane) (Q-PDMS) 4-Armed Star Polymer, Attempted Desilylation of Model Phenyl-tris(PDMS) 3-Armed Star Polymer with Monofunctional TMAS to obtain tetrakis(PDMS) 4-Armed Star Polymer (Q-PDMS), Preparation of Samples for Monitoring of the Course of the Silanolate-Initiated Polymerization of Cyclic Siloxanes), *Results and Discussion* (Overview of Synthesized Vinylsilyl-Terminated α,ω -Telechelic Terpolysiloxanes, DiPhS-Containing Polymers, DiEtS-Containing Polymers, Monitoring of the Course of the Ring Opening Polymerization of Cyclic Siloxanes during Preparation of Vinylsilyl-Terminated α,ω -Telechelic Terpolysiloxanes, MePhS-Containing Polymers), *Conclusions* and *References*. In addition to the text of the dissertation, the candidate has also included the Biography and Supplements required by the University's rules on submitting the doctoral dissertations for approval. By its form and content, the text meets all the standards of the University of Belgrade for doctoral dissertation.

2.2. Brief review of individual chapters

The **Introduction** chapter reviews the subject, content, objectives and significance of the research, which include the development of new, linear and completely amorphous vinyl-functionalized terpolysiloxanes. Such linear copolysiloxanes would be especially suitable as precursors for the preparation of low temperature elastomers, and at present are at the center of attention as candidates for the first elastomeric materials for application in three-dimensional (3D) printing. The subject of the investigation included the synthesis and characterization of several series of random terpolysiloxanes based on dimethylsiloxy (DiMeS), diphenylsiloxy (DiPhS), diethylsiloxy (DiEtS) or methylphenylsiloxy (MePhS), and methylvinylsiloxy (MeViS)

repeat units with terminal dimethylvinylsiloxy (DiMeViS) groups. These polymers were prepared by anionic ring opening polymerization (ROP)-equilibration of different mixtures of cyclic siloxanes, including octamethylcyclotetrasiloxane, D_4 , octaphenylcyclotetrasiloxane, D_4^{Ph2} , tetramethyltetraphenylcyclotetrasiloxane, D_4^{MePh} , octaethylcyclotetrasiloxane, D_4^{Et2} , hexaethylcyclotrisiloxane, D_3^{Et2} , and tetramethyltrivinylcyclotetrasiloxane, D_4^{MeVi} , initiated with oligodimethylsiloxy tetramethylammonium disilanolate, TMAS, in the presence of α,ω -telechelic dimethylvinylsiloxy-terminated oligodimethylsiloxane, end-blocker, DiViEB. Polymerization reactions were carried out in bulk. The degree of polymerization (DP) of terpolysiloxanes was controlled by the molar ratio of molecular weight regulator, DiViEB, and siloxy units introduced with the cyclic monomers and varied between 80 and 600. DiPhS, DiEtS and MePhS residues, the role of which was to suppress the crystallization of polydimethylsiloxane (PDMS), were incorporated into polymers in the amounts from 3 to 7 mol %. Particular attention was paid to the elucidation of the mechanism of chain branching in DiPhS-containing copolymers. A significant segment of the research was focused on the development and application of practical methods for monitoring selected parameters of the polymerization reactions in these systems, including molecular weight and yield of polymer, monomer conversion, as well as the microstructure of the polymer. The most complex of all the investigated systems, the copolymerization of D_4 and D_4^{Ph2} , which, in addition to the complexity induced by simultaneous occurrence of the ROP and the equilibration reactions, also featured an additional aspect of the initial heterogeneity of the mixture of two very differently reactive cyclic monomers.

Theoretical part of the doctoral dissertation consists of eight sections. The first section (*Overview*) provides a very brief look at the content of the chapter. In the second section (*Chemistry of Organosiloxanes-Historical Background*) the sequence of research achievements in the field of organosiloxanes is described, which, thanks to the industrial interest and the development that began in the 1930s, led to the commercialization and launching of the first polysiloxane during World War II. In the third section (*Siloxane Bond*), the electronic configuration of the siloxane bond is described in detail, together with the physical and chemical properties of polysiloxanes arising from it; the application of polysiloxanes is also described with particular reference to the application in modern 3D printing technology. In the fourth section (*Synthesis of Polysiloxanes*), procedures for the preparation of organochlorosilanes, precursors for the synthesis of polysiloxanes, as well as the methods of preparing linear polysiloxanes starting from diorganodichlorosilanes are reviewed. In the fifth section (*Synthesis of Polysiloxanes via Ring Opening Polymerization of Cyclic Siloxanes*), the previous investigations on anionic and cationic polymerizations of cyclosiloxanes are described in detail, with special attention dedicated to kinetic and thermodynamic control of anionic processes as well as thermally degradable (transient) basic initiators. The sixth section (*Crystallization of polysiloxanes*) included a review of the literature related to the crystallization of polysiloxanes and its suppression. Possibilities for characterization of microstructure and architecture of polysiloxanes that offers ^{29}Si NMR spectroscopy are presented in the seventh section (^{29}Si NMR

Spectroscopy: A Powerful Tool for Structural Analysis of Polysiloxanes). The eighth section (*Size Exclusion Chromatography*) provides a summary overview of the molecular parameters that can be obtained by applying this separation technique in combination with light scattering detection, refractometry and on-line viscometer.

In the **Experimental** part, the materials used for the preparation of terpolysiloxanes, initiators, model branched polymers and molecular weight regulator are reported, followed by the description of the methods used to characterize synthesized products. The chapter also contains detailed description of syntheses of the initiators α,ω -*bis*tetramethylammonium-oligodimethylsiloxylate (TMAS) and tetramethylammonium-oligodimethylsiloxysilanolate (monoTMAS), α,ω -dimethylvinylsiloxyl end-blocker (DiViEB), vinyl-terminated terpolysiloxanes, model, star branched polymers phenyl-*tris*(polydimethylsiloxane) (Ph-T-PDMS) and *tetrakis*(polydimethylsiloxane) (Q-PDMS), attempted desilylation of model Ph-T-PDMS by monoTMAS to obtain Q-PDMS, as well as preparation of samples for monitoring of the course of the silanolate-initiated polymerization of cyclic siloxanes.

Results and Discussion are organized in five sections. In the first section (*Overview of Synthesized Vinylsilyl-Terminated α,ω -Telechelic Terpolysiloxanes*), three series of α,ω -telechelic dimethylvinylsiloxyl-, $\text{CH}_2=\text{CH}-\text{Si}(\text{CH}_3)_2\text{-O-}$, terminated terpolysiloxanes containing different relative amounts of Me, Ph, Et and Vi side groups, prepared using the TMAS-initiated anionic ROP, are defined. The section also contains the results of the characterization of all terpolymers (iodometry, SEC-MALS-VIS, viscometry, NMR spectroscopy).

In the second section (*DiPhS-Containing Polymers*) evaluation of two series of synthesized terpolysiloxanes containing 3.6 mol% DiPhS repeat units is described. The first series included 4 polymers in which targeted degrees of polymerization (DP) varied in the range from 80 to 600, by varying the amount of added DiViEB, while the molar ratio of DiViEB and TMAS ([DiViEB]/[TMAS]) was kept constant: 2/1. In another series of 6 polymers [DiViEB]/[TMAS] ratio varied from 20/1 to 1/1, while the targeted DP remained constant (DP = 160). DSC measurements showed that the addition of 3.6 mol% of DiPhS units completely prevented crystallization of PDMS. Based on results from ^{29}Si NMR and SEC-MALS-VISC analyses, it was found that chain branching occurred in these polymers. Since ^{29}Si NMR spectra of the investigated polysiloxanes showed a signal at -80 ppm, assigned to phenyl trisiloxyl silicon (Ph-T), whose intensity (relative to intensity of signal from DiPhS monomer units) increases with TMAS concentration, a branching mechanism was proposed for DiPhS-containing terpolysiloxanes. Proposed mechanism of branching encompasses the nucleophilic attack by silanolate on the polar side Si-C_{Ar} bonds from the DiPhS units and the subsequent replacement of the phenyl groups by polysiloxane chains, resulting in the formation of Ph-T and Q monomer units (branching points). ^{29}Si NMR characterization of the synthesized model branched polymers, phenyl-*tris*(polydimethylsiloxane) (Ph-T-PDMS) and *tetrakis*(polydimethylsiloxane) (Q-PDMS), confirmed the validity of the assumption of the formation of Ph-T branch units (^{29}Si NMR signal at -80 ppm) and the absence of quaternary, Q, branch units, respectively, in DiPhS-

containing polymers. The attempt to desilylate the Si-C_{Ar} bond of the model-branched polymer (Ph-T-PDMS) did not lead to the formation of the Q structures, demonstrating experimentally that the branching mechanism in the investigated terpolysiloxane does not imply total desilylation of the DiPhS groups. SEC-MALS-VISC analysis showed that, due to the occurrence of side reaction of desilylation which leads to branching, the number-average molecular weights of the synthesized terpolysiloxanes were far greater than targeted, and that their polydispersity dramatically increased with the concentration of the initiator. The SEC-MALS-VISC measurements also enabled determination of the value of the exponent a from the Mark-Houwink-Sakurada (MHS) equation ($[\eta] = KM^a$) which bears information on conformation of polymer chains. For most of DiPhS-containing terpolysiloxanes the value of MHS exponents a , were less than 0.5, pointing at the pronounced compactness of macromolecules, typical for branched polymers.

In the third section (*DiEtS-Containing Polymers*), the development of new terpolysiloxanes, in which DiPhS units were replaced with DiEtS ones, is presented. The underlying hypothesis was that the replacement of the lateral phenyl groups in copolymers with large and bulky ethyl groups would equally well suppress their crystallization while simultaneously preventing chain branching by reducing electrophilicity of phenyl-substituted silicon and decreasing its susceptibility to the nucleophilic attack by active silanolate species. Three series of polysiloxanes were prepared using different sources of DiEtS units: a) hexaethylcyclotrisiloxane, D₃^{Et2}, b) octaethylcyclotetrasiloxane, D₄^{Et2} and c) DiEtS hydrolyzate, which represents a commercial mixture of cyclic siloxanes and linear polydiethylsiloxane, PDES, of a moderately high molecular weight (ca. 17,000). While all the polymers prepared with pure D₃^{Et2} and D₄^{Et2} showed the absence of crystallinity, the attempt to suppress crystallization of PDMS by using DiEtS-hydrolyzate failed. ²⁹Si NMR analysis of the latter revealed presence of longer PDES blocks (signal at -23 ppm) arising from the linear fraction of DiEtS-hydrolyzate, which did not effectively participate in equilibration reactions. SEC-MALS-VISC analysis confirmed complete linearity of all DiEtS-containing polymers: molecular weights in the targeted range, a polydispersity of 1.5 to 2, typical for fully equilibrated linear polysiloxanes and conformation in diluted solutions characteristic of linear polymers in thermodynamically good solvent.

In the fourth section (*Monitoring of the Course of the Ring Opening Polymerization of Cyclic Siloxanes during Preparation of Vinylsilyl-Terminated α,ω -Telechelic Terpolysiloxanes*), the dynamics of anionic polymerization of cyclosiloxanes in terpolymer systems containing DiPhS and DiEtS repeat units as well as in the reference system, PDMS homopolymer, is discussed. Progress of reactions was monitored using SEC, ²⁹Si NMR and TGA methods. While homopolymerization of D₄ and copolymerization of D₄ with D₃^{Et2} occurred in a practically identical manner with the characteristic rapid growth of the polymer and its yield, the copolymerization of D₄ with D₄^{Ph2} involved a distinct "induction period" as a consequence of reduced miscibility of monomers and a significantly higher reactivity of D₄^{Ph2} than D₄ towards dimethylsilanolate. A new mechanism for the copolymerization of D₄ with D₄^{Ph2} was proposed which includes: a) initial formation of B-A-B triblocks of DiMeS (A) and DiPhS (B) segments,

followed by b) formation of A-B-A-B-A pentablock species, and c) redistribution of the multiblocks through a siloxane equilibration reaction into copolymers containing single DiPhS units separated by extended PDMS sequences.

As analysis of branching in DiPhS-containing terpolysiloxanes demonstrated and experiments with model, Ph-T-branched PDMS confirmed, desilylation of DiPhS unit which would lead to the formation of Q branch point *did not* proceed beyond the Ph-T-branch stage since silicon atoms from phenyl-T units were less susceptible to nucleophilic attack than the silicon atoms from diphenylsiloxy units. Based on these results, it is postulated in the fifth section (*MePhS-Containing Polymers*) that terpolysiloxanes containing the methylphenylsiloxy (MePhS) repeat units should be completely resistant to the nucleophilic attacks by silanolates maintaining perfectly linear chain configuration while simultaneously suppressing crystallization of PDMS. Characterization of the synthesized MePhS-containing terpolysiloxanes (^{29}Si NMR, SEC-MALS-VISC) confirmed that they retained both amorphousness and linearity of chains, thus proving the correctness of said postulates. Monitoring experiments showed that MePhS-containing system, similar to homopolymerization of D_4 and copolymerization of D_4 and $\text{D}_3^{\text{Et}2}$, exhibited rapid growth of the polymer and its yield, as well as highly efficient randomization of MePhS units along the polymer chains.

Chapter **Conclusions** summarizes the most important conclusions drawn from the investigation presented in the preceding chapters.

Chapter **References** contains literature references cited in the dissertation as well as publications derived from the research presented in the dissertation.

3. THE ASSESSMENT OF DISSERTATION

3.1. Originality

Due to the unusual combination of exceptional properties over a wide range of temperatures, including: flexibility, exceptional thermal and thermoxidative stability, unique surface properties, optical transparency, high gas permeability, biocompatibility, etc., polysiloxanes are traditionally widely used in many areas. In recent years, the application of polysiloxane elastomers in 3D printing, defined as the precise technology for the creation of customized, complex three-dimensional objects of delicate geometry and microarchitecture from digital files, has attracted great attention of both academia and industry. These methods of applying layer by layer of polymeric material enable new ways of precise manufacturing of functionalities and/or improved material performance, which is impossible to achieve by traditional methods of elastomer processing. Along with the rapid advancement of 3D printing technology, industrial demand for well-defined functional polysiloxanes which would enable precise manufacturing of complex features is progressively increasing, in order to expand their application.

Inherent chain flexibility of polysiloxanes, derived from unusually long siloxane bond, large bond angle of Si-O-Si linkage as well as very low intersegmental interactions, makes them potentially perfect candidates for precursors for low-temperature elastomers. The major drawback, despite remarkable elasticity at extremely low temperatures, is their strong tendency towards crystallization, which dramatically narrows the temperature range of usefulness. In the case of polydimethylsiloxane, PDMS, commercially the most representative member of this polymer group, complete suppression of crystallization is easily achieved by the substitution of small amounts of lateral methyl groups with large and bulky phenyl groups. Another critical aspect for the successful application of siloxane elastomers includes a well-defined, regular network structure. It is therefore necessary for synthetic strategies for the preparation of precursors for polysiloxane networks to be focused on achieving both linearity and uniform functionalization of precursor. Nonlinearity of precursors due to chain branching would lead to the formation of network imperfections, such as elastically inactive dangling chains. For this reason, in order to provide the predictable rubber elasticity of the siloxane elastomer at extremely low temperatures, it is necessary to eliminate the possibility of chain branching while simultaneously suppressing the polymer crystallization.

According to the aforementioned, the research conducted within this doctoral dissertation was focused on studying the effect of the structure of various cyclic siloxanes on linearity and thermal transitions of their polymers with the aim of developing well-defined precursors suitable for use in low-temperature elastomers. Towards this end, several series of random, vinyl-functional copolysiloxanes were synthesized, which beside dominant, dimethylsiloxy-, DiMeS, also contained statistically distributed small amounts (3-7 mol%) of diphenylsiloxy-, DiPhS, or diethylsiloxy-, DiEtS, or methylphenylsiloxy-, MePhS, repeat units, using anionic ring opening polymerization of cyclic siloxanes. While by random incorporation of each of the above mentioned bulky comonomers PDMS-like crystallization was successfully suppressed, providing complete amorphousness of material, it was found that Si-C_{Ar} side bonds of DiPhS-containing polymers easily undergo reaction of desilylation in the presence of the nucleophilic initiator (silanolate), resulting in branching of the chains. It was also demonstrated that the chain branching mechanism in these polymers does not imply a total desilylation, as the substitution of the first Ph group in the DiPhS segment by the polysiloxane chain significantly reduces the silicon electrophilicity, as well as its susceptibility to the subsequent nucleophilic attack.

A significant portion of the research was focused on the development and application of practical methods of monitoring selected parameters of the polymerization reaction in these systems, which include molecular weight and yield of polymer, conversion of monomers, as well as the microstructure of polymer. Particular attention was devoted to the most complex system, the copolymerization of D₄ and D₄^{Ph2} monomers, which includes a characteristic induction period due to the very low degree of miscibility and significant differences in the reactivity of these monomers toward silanolate. Based on chromatographic, spectroscopic and results of thermal degradation analysis obtained from these experiments, a new three-step reaction mechanism was proposed describing the dynamics of copolymerization in this complex system. In contrast to

this, the processes in systems prepared with $D_3^{Et_2}$ and D_4^{MePh} comonomers were characterized by very rapid growth of molecular weight and polymer yield, as well as highly efficient redistribution of monomer residues. The fact that such effective preparation of completely amorphous terpolysiloxanes containing DiEtS or MePhS monomer units also completely eliminates the possibility of chain-branching makes them ideal candidates for precursors of low temperature elastomers.

3.2. Review of referenced and used literature

The doctoral dissertation contains 208 literature citations, related to the research of relevance to the issues addressed in the dissertation. Reviewed literature refers to a) chemistry of siloxanes with particular emphasis on ring-opening polymerization of cyclic siloxanes, and kinetic and thermodynamic control of the process, b) polysiloxanes' crystallization phenomenon and synthetic strategies for its suppression and c) modern methods of characterization of polysiloxanes. By reviewing and analyzing the current literature sources related to all parts of the dissertation, the candidate has contributed to deeper understanding of already present knowledge in the areas of synthesis, characterization and application of polysiloxanes. It can be concluded from the list of references that the candidate follows and properly understands the current trends in the field of research related to this doctoral dissertation.

3.3. Description and adequacy of applied scientific methods

The investigations conducted within this doctoral dissertation entailed the implementation of appropriate original or modified methods for the synthesis of terpolysiloxanes, initiators, molecular weight regulators and model branched polymers, as well as modern experimental characterization techniques, used to confirm the initial assumptions. Anionic ring-opening polymerization (A-ROP) of cyclic siloxanes, initiated by tetramethylammonium silanolate (TMAS), was applied for the preparation of terpolysiloxanes. The molecular weight regulator and model branched polymers were synthesized by low-temperature cationic ring-opening polymerization (C-ROP) of D_4 in the presence of the ion-exchange resin Amberlyst 15. The initiator tetramethylammonium silanolate (TMAS) was synthesized by reaction of tetramethylammonium pentahydrate ($(CH_3)_4NOH \cdot 5H_2O$) and D_4 in which reaction-generated and water of hydration was removed by azeotropic distillation in the presence of cyclohexane.

Molecular weights, molecular weight distribution, the size and conformation of the synthesized polymers were determined using size exclusion chromatography coupled with multi-angle light scattering detector, on-line viscometer and differential refractometer (SEC/MALS/VIS/RI). The conversion of monomers during polymerization was evaluated based on the results of size exclusion chromatography with the refractive index detection. The composition and microstructure of the synthesized polymers and initiators were studied using nuclear magnetic resonance (1H NMR, ^{29}Si NMR). The melting and crystallization temperatures of the synthesized

polymers were determined using differential scanning calorimetry (DSC). The relative ratio of the cyclic and linear components (yield of the polymer) was determined by the thermogravimetric analysis (TGA) of the reaction mixture samples taken at different reaction times. Dynamic viscosity of the isolated polymer samples was measured using a rheometer with cone/plate geometry. The content of vinyl groups in the prepared polymers and oligomers was determined by iodometric titration.

3.4. Applicability of the achieved results

Since the application of siloxane elastomers in 3D printing technology has been in the focus of recent academic and industrial interest, the results of the research carried out within this doctoral dissertation have made a significant contribution towards the development of well-defined, linear polysiloxane precursors which retain their elasticity at extremely low temperatures. Particularly important are the fundamental findings that have emerged during these studies, related to new proposed branching and copolymerization mechanisms in complex systems involving DiPhS monomer units. These new findings have provided a deeper insight into the structure and properties of the considered copolymers, and enabled the development of several types of terpolysiloxanes of different composition for elastomer precursors of the required quality. Scientific verification of the results of this doctoral dissertation was confirmed in papers published in international journals of exceptional value.

3.5. Assessment of the competency of the candidate for independent scientific work

During the preparation of this doctoral dissertation candidate Alisa Zlatanić, M.Sci., has demonstrated outstanding expertise and independence in the search and use of scientific literature, planning, design and implementation of experiments, processing and interpretation of the data obtained, discussion of the results and preparation of publications. She has also upgraded the existing knowledge in the field of synthesis and characterization of polymers by mastering various procedures for the synthesis of polysiloxanes, as well as modern experimental techniques for the characterization of polymers. Considering her previous efforts and achieved results, as well as the content of the submitted doctoral dissertation, the Committee has determined that the candidate possesses all the qualities necessary for independent scientific research.

4. SCIENTIFIC CONTRIBUTION

4.1. Review of the realized scientific contributions

Within the framework of her doctoral dissertation, candidate Alisa Zlatanić, has made a significant contribution towards the development and evaluation of new vinyl-functional

polysiloxane precursors for elastomers with improved structure, thermal and mechanical properties. The scientific contributions of the accomplishments achieved during the preparation of this doctoral dissertation include:

- Determination of detailed reaction mechanism behind the chain-branching occurring during preparation of DiPhS-containing terpolysiloxanes by anionic ring-opening polymerization of cyclic siloxanes;
- Quantification of the extent of branching in DiPhS-containing terpolysiloxanes of different degrees of polymerization (DP);
- Determination of critical concentration of the silanolate at which branching occurs during the synthesis of DiPhS-containing terpolysiloxanes;
- Comparison of the efficiency of the substitution of methyl groups with ethyl groups using three types of diethylsiloxane monomers: D_3^{Et2} , D_4^{Et2} and DiEt hydrolyzate;
- Evaluation of the possibility and efficacy of preventing crystallization and branching of terpolysiloxanes by replacing DiPhS repeat units with DiEtS and MePhS analogues;
- Determination of minimum levels of incorporation of DiEtS or MePhS segments in linear terpolysiloxanes leading to complete suppression of crystallization;
- Determination of the mechanism of anionic copolymerization of diphenyl and dimethyl substituted cyclic siloxanes.

4.2. Critical analysis of research results

After detailed analysis of the state of the research in the considered field, the investigations presented in this doctoral dissertation were designed with two main goals: a) the development of new, fully amorphous and strictly linear polysiloxanes, suitable for extreme low temperature applications, and b) comprehensive evaluation of the process of obtaining such polymers by anionic ring opening polymerization (ROP) of selected cyclosiloxanes in bulk. The properties and performance of crosslinked elastomers primarily depend on the structure and architecture of polysiloxane precursors used for their preparation. In order to preserve the rubberlike elasticity of siloxane elastomers at extremely low temperatures and thereby attain a wide temperature range of their usefulness, it is necessary to eliminate crystallinity in their polysiloxane precursors. It is also necessary to provide the linearity of the polysiloxane chains to prevent, or at least minimize, the presence of network imperfections in the form of elastically inactive dangling chains, which disrupt the regularity of crosslinked structure, and thus the mechanical properties of the elastomer. In accordance with the established goals, the research conducted in this doctoral dissertation resulted in a) elucidation of the mechanism of chain-branching occurring in diphenyl substituted polysiloxanes during anionic polymerization of cyclosiloxanes, b) determination of critical concentrations of silanolates for the onset of chain-branching in DiPhS-containing systems, c) demonstration of the possibility and effectiveness of suppression of crystallization and branching in polysiloxanes by replacing DiPhS unit with their DiEtS and MePhS analogues,

and d) proposal of a new mechanism of anionic copolymerization of D₄ and D₄^{Ph₂} monomers, which explains the delayed start of reaction in the investigated system.

By comparing the set goals with the achieved results, the Committee concluded that the completed research fully meets the criteria of the doctoral dissertation. Based on the contemporary methods of research and analysis applied in this dissertation, it was concluded that the results achieved were of great importance not only from the scientific but also from the practical point of view.

4.3. Verification of scientific contributions

Candidate Alisa Zlatanić has achieved significant results in the field of research referred to in this doctoral dissertation, which have been also verified in papers published in internationally relevant journals and presented at scientific conferences. Two full scientific papers from this doctoral dissertation were published in international journal of excellence (M21a) and one paper in the top international journal (M21). Parts of the research results were also presented at national scientific meetings (M64).

Category M21a (Paper in international journal of excellence)

1. **Zlatanic, A.**, Radojic, D., Wan, X., Messman, J. M., Dvornic, P. R., *Monitoring of the Course of the Silanolate-Initiated Polymerization of Cyclic Siloxanes. A Mechanism for the Copolymerization of Dimethyl and Diphenyl Monomers.* *Macromolecules* 51, 895-905 (2018) (ISSN: 0024-9297, IF(2017): 5,914)
2. **Zlatanic A.**, Radojic D., Wan X., Messman J. M., Dvornic P. R., *Suppression of Crystallization in Polydimethylsiloxanes and Chain Branching in Their Phenyl-Containing Copolymers.* *Macromolecules*, 50, 3532-3543 (2017) (ISSN: 0024-9297, IF(2016): 5,835)

Category M21 (Paper in top international journal)

1. **Zlatanic A.**, Radojic D., Wan X., Messman J. M., Bowen D. E., Dvornic P. R., *Dimethyl-Methylphenyl Copolysiloxanes by Dimethylsilanolate-Initiated Ring Opening Polymerization. Evidence for Linearity of the Resulting Polymer Structures,* *Journal of Polymer Science Part A: Polymer Chemistry*, DOI: 10.1002/pola.29367 (2019), (ISSN: 0887-624X, IF(2017):2,588)

Category M64 (Work presented at national scientific meetings)

1. **Zlatanic A.**, Radojic D., Wan X., Messman M. J., Dvornic R.P., *Synthesis and Characterization of Polysiloxane Terpolymers Containing Methyl, Ethyl, Phenyl and Vinyl Siloxy Units,* 43rd Polymeric Materials, Adhesives, and Composites Conference (PolyMAC), Kansas City, MO, June 14–16, 2016.

2. Radojčić D., **Zlatanić A.**, Wan X, Messman M. J., Dvornić R. P., *Quantitative Analysis of Microstructure in Dimethylvinyl Terminated Dimethyl, Diphenyl, MethylVinyl Containing Siloxane Copolymers by ²⁹Si NMR*, 51st Midwest Regional ACS Meeting, Manhattan, KS, October 26-28, 2016.
3. Wan X., **Zlatanić A.**, Messman M. J., Dvornić R.P., *Characterization of Molecular Weights and Structures of Polysiloxanes by SEC with Triple Detection Capability*, Pentasectional Regional ACS Meeting, Bartlesville, OK, April 8-9, 2016.
4. **Zlatanić A.**, Radojčić D., Wan M., Bergman E. J., Messman M.J., Bowen E.D., Dvornić R.P., *Synthesis and Characterization of Silicone Gum Precursors*, Silicone Summit, Kansas City, MO, November 10-12, 2015.

The candidate is also a co-author of one paper published in the top international journal (M21) related to the application of terpolysiloxanes developed during the preparation of this doctoral dissertation in 3D printing technology.

Category M21 (Paper in the top international journal)

1. Surrine, J. M.; **Zlatanić, A.**; Meenakshisundaram, V.; Messman, J. M.; Williams, C. B.; Dvornić, P. R.; Long, T. E. 3D Printing Amorphous Polysiloxane Terpolymers via Vat Photopolymerization. *Macromolecular Chemistry and Physics* 220, 1800425 (2019) (ISSN: 1521-3935, IF(2018): 2.492)

5. CONCLUSION AND PROPOSAL

Based on the presented material, the Committee concluded that the doctoral dissertation of Alisa Zlatanić represents an original scientific contribution in the field of synthesis and characterization of polysiloxanes. Novel, completely amorphous and linear vinyl-functional terpolymers prepared by anionic polymerization of cyclosiloxanes were fully characterized in terms of microstructure, size and distribution of molecular weights, thermal and rheological properties, as well as the content of vinyl functional groups. By elucidating both chain-branching and mechanism of copolymerization reaction in diphenyl-substituted systems, a valuable contribution has been made in studying the effect of structure of monomers on the properties of polysiloxane and the course of their polymerization reactions. Having considered the quality, the scope and the scientific contribution of the achieved results, the Committee proposes to the Scientific and Academic Council of the Faculty of Technology and Metallurgy of the University of Belgrade to accept this Report and, together with the submitted dissertation of Alisa Zlatanić, M.Sci., entitled „The Effect of Structure of Cyclic Monomers on the Course of Anionic Polymerization and Properties of Vinyl-Terminated Polysiloxanes (Uticaj strukture cikličnih monomera na tok anjonske polimerizacije i svojstva vinil-terminiranih polisiloksana)“ announce

it in public and, after the expiration of the deadline required by law, refer to the final approval of the Professional Board for Natural Sciences of the University of Belgrade, and upon completion of this procedure, invite the candidate to the oral defense of the doctoral dissertation before the same Committee.

In Belgrade, 15.04.2019.

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