STUDIES ON THE ELECTROSPINNABILITY OF POLYMER SUPRAMOLECULES

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INDIAN INSTITUTE OF TECHNOLOGY DELHI

February 2021

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by

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Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

February 2021

DEDICATED WITH EXTREME AFFECTION AND GRATITUDE TO

my parents Mr. Kedar Malpani and Mrs. Radha Malpani

CERTIFICATE

This is to certify that the thesis titled **'Studies on the Electrospinnability of Polymer Supramolecules'**, being submitted by **Ms. Deepika Malpani** to the Indian Institute of Technology Delhi, for the award of ***Doctor of Philosophy***, is a record of bonafide research work carried out by her. She has worked under our guidance and supervision and fulfilled the requirements for the submission of thesis which has attained the standard required for a PhD. degree of this Institute. The work carried out to complete this thesis has not been submitted for the award of degree or diploma in any institute in part or full.

(Prof. Bhanu Nandan)	**(Prof. Rajiv K. Srivastava)**
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ACKNOWLEDGEMENTS

In the successful accomplishment of this project, many people have best owned upon me their blessings and the heart pledged support. I am utilizing this time to thank to all those who have contributed to this project.

Primarily, I express my gratitude and sincere thanks to Almighty from bottom of my heart for blessing me with my two supervisors Prof. Bhanu Nandan and Prof. Rajiv K. Srivastava, for supporting the idea and giving me opportunity to undertake this work. Their motivation skills, constant guidance, and timely suggestions always helped me during the tenure of this research work. I shall be grateful to them for their invaluable suggestions and untiring help, which they always showed right from the beginning till the successful completion of this endeavour.

I am highly grateful and thankful to my ex-managers Mr. Dharmesh Gala and Mr. Rishi Kaushik, from my earlier employer Anton Paar Pvt. Ltd., for their constant encouragement and guidance. I appreciate their efforts, support and time given to me to pursue this Ph.D and utilizing their lab facilities as and when required to carry out my research work while working with them.

I feel immense honour and pride to acknowledge Indian Institute of Technology Delhi, New Delhi for providing me excellent environment and facilities throughout my research period. I would also like to thank the all the Heads of the Department of Textile Technology since 2015, for providing infrastructure facility and cooperation for smooth completion of this research work. Further, I would like to express gratitude and sincere thanks to my SRC members: Prof. Ashwini Agarwal, Prof. Bhupendra Singh Butola and Prof. Paresh Chowksi for their valuable inputs and suggestions during the course of this work.

I am thankful to CRF and NRF analytical facilities and SMITA research facility of IIT Delhi for providing me access to various characterization instruments which were required for my studies. My special thanks to the Lab Technicians and other staff members of our Department, Mr. Kuldeep, Mr. Mahesh, Miss Astha, Mr. R. Khattar, Mr. Amarjeet, Mr. V. K. Kala, and Mr. Subhash for extending their extensive and timely help whenever asked for.

I am also thankful to Prof. Siddharth Pandey for giving me access to use surface tension analysis equipment from his lab, which was a crucial analysis for my research. Moreover, I am thankful to Prof. Manfred Stamm and Dr. Andriy Horechyy, Leibniz Institute for Polymer Research, Dresden, Germany for providing access to SAXS facilities.

I also would like to extend my warm thanks to my current manager Dr. Sumanda Bandyopadhyay, SABIC Research and Technology Pvt. Ltd., Bangalore, for his constant words of encouragement and guidance and for allowing me to utilize SABIC's lab facilities in carrying out my research work whenever needed. Besides, I would also like to thank my colleagues Dr. Radha Kamlakaran, M.B. Pallavi, Dr. Shweta Hegde, from my current employer SABIC Bangalore, for extending their immense support with the analyses i.e. SEM, TEM, BET, etc. whenever required for my research work.

Peer group learning has been a great lesson to me in our Department, where the students are incredibly talented and resourceful, and help each other a lot during the course of experiments as well as while analyzing the raw data. I would like to extend my thanks to my fellow labmates, Sanchayan, Sumana, Sajan, Avinash, Ashish, Dr. Asheesh, Dr. Puhup, Dr. Khushboo, Dr. Kalyan, Anil, Pramod, Dr. Pratick, Labeesh, and Asha for their immense distant help whenever needed. I would also like to thank my friends Prateek, Dr. Sanjeev, Dr. Safeer, Dr. Satyanarayan, Dr. Achala, Chhavi, Anuradha and Neeraj, for their extensive and timely help whenever required. I would like to extend my special thanks to my dear friend Dr. Sanchi and Neeta who always helped me out of the way and have made this tenure smooth.

Last but not the least, I would like to thank my parents who have taught me to be hard working and devoted in life, and for supporting me emotionally and with love which highly boosted my energies and enthusiasm towards my Ph.D all these years. My sisters and brother have always supported me with their unconditional love and care and my deep regards are always with them who have been with me when times are rough.

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ABSTRACT

Entanglements are the desirable feature for a solution to be electrospinnable. A lot of strategies have been employed with the focus to improve the electrospinnability of the otherwise not readily electrospinnable polymer solutions. Among the various strategies the ones involving supramolecular interactions have been quite captivating and compelling. Supramolecular interactions basically involve non-covalent complexation of the simple building blocks to result in the formation of a complex and functional materials. To widen the scope of the applicability of the electrospinning technique to fabricate nanofibers, a robust route of supramolecular interactions between polymer/surfactant is proposed for rigid/semirigid polymers with otherwise limited applicability to the electrospinning technique. The one of the most common polymer candidates, used as a component for supramolecular interaction, is the Poly(4-vinyl pyridine) (P4VP). The side chain pendent groups of P4VP can interact with many functional molecules, via multiple interactions namely electrostatic, hydrogen bonding, coordination bonding etc. Hence, it is necessary to understand the role of interaction strength of such supramolecular interactions on solution rheology and electrospinnability. In the current thesis work, the supramolecular assemblies of P4VP, bonded via various interactions with amphiphiles namely dodecylbenzenesulfonic acid (DBSA), 3-pentadecylphenol (3-PDP) and Zn salt of dodecylbenzenesulfonic acid ($Zn(DBSA)_2$), bearing different chemical head groups are explored. The interaction between such amphiphiles with polymer result in supramolecular comb polymers and the dangling alkyl tails undergo non-polar interactions, resulting in polymer interchain associations. Thus, amphiphiles functional heads with different interaction strength also determine the stability of such polymer interchain associations facilitated by the non-polar alkyl tails dangling with amphiphiles. This consequently impacts the rheological properties and electrospinnability. Moreover, such supramolecular comb polymers have propensity to self organize in hierarchal structures, which on selective removal of amphiphiles may avail porous/ channeled structures for potential applications.

To this end, for the current work, complexes of varying interaction strengths between P4VP and amphiphiles/surfactants were prepared. The 3-pentadecylphenol (3-PDP) interacts *via* hydrogen bonding, the dodecylbenzenesulfonic acid (DBSA) interacts with P4VP *via* ionic bonding whereas, the Zn salt of dodecylbenzenesulfonic acid (Zn(DBSA)$_2$) interacts through coordination bonding. The respective interactions were confirmed by FTIR and solution properties were determined. The supramolecular interactions based on hydrogen bonding were found to be too dynamic to influence the electrospinnability of the P4VP/PDP complexes significantly. This plausibly was due to the temporal nature of the hydrogen bonds in solution because of which the relaxation time of the physical network formed was much shorter. These supramolecular comb polymers of P4VP/PDP complexes further demonstrated their typical mesomorphic structure in the electrospun nanofibers and were characterized by SAXS and DSC. Moreover, the PDP could be selectively removed from the electrospun nanofibers due to their weak interaction with polymer, resulting in the formation of porous nanofibers. Whereas, on the contrary, a prominent impact on viscoelastic properties were found at low molar ratios of 0.05 itself for P4VP(DBSA)/DMF complex solutions involving ionic interactions. The increase in the viscosity for the P4VP/DBSA complexes was plausibly due to stronger interaction strength of ionic bonds as compared to the hydrogen bonds. Hence, the networks formed in P4VP/DBSA system were likely to relax more slowly due to the more stable interchain associations. The P4VP(DBSA)/DMF complex solutions could be electrospun at very low concentration of 12 wt% itself which otherwise was not possible till even 35 w% in case of neat P4VP. Furthermore, the SAXS analysis showed that electrospun nanofibers exhibited significantly improved lamellar order than bulk film, which was plausibly facilitated by the preferred orientation of P4VP chains along the fiber axis. The significance of ionic interactions and non-polar associative interactions of alkyl tails, was further evident from the fact that both the rheological properties as well as electrospinnability were not enhanced to the same extent in the case of P2VP/DBSA and P4VP/BSA complexes, where either the ionic interactions were weak or the non-polar alkyl tail interactions were absent. Among all the complex solutions, the P4VP(Zn(DBSA)$_2$/DMF complexes led to a profound increase in the viscoelastic properties at a molar ratio as low as 0.01 itself. This was mainly due to the fact that the Zn(DBSA)$_2$ molecules can bind to multiple 4VP units at a time through coordination interaction, which further enable interchain associations through non-

polar interactions of dangling tails. Such multipoint interactions between chains result in rich rheological properties of these complex solutions. The P4VP/Zn(DBSA)$_2$ complex solutions at higher molar ratios were found to follow the scaling laws described by sticky Rouse and sticky reptation models. Furthermore, the universality of combining multiple associative interactions, on electrospinnability, was evident from the fact that both the rheological properties as well as electrospinnability were not improved to the same extent in the case of poly(2-vinylpyridine) (P2VP)/Zn(DBSA)$_2$ and P4VP/Zn(BSA)$_2$ (zinc salt of benezenesulfonic acid) complexes, where either the coordination interactions were weak or the non-polar alkyl tail interactions were absent. Thus, overall, the present work reports a comprehensive fundamental study on the supramolecular approach for improving electrospinnability which could be applicable for a number of rigid/semi-rigid polymers. Furthermore, the approach could also be extended to produce porous and functional electrospun nanofibers.

सार

बहुलक के इलेक्ट्रोलस्पिनिबल होने के समाधान के लिए बहुलक अणुओ में उलझन एक वांछनीय विशेषता है। अन्यथा आसानी से इलेक्ट्रोस्पिनिबल नहीं होने वाले बहुलक में इलेक्ट्रोलस्पिनिबिलिटी में सुधार के लिए बहुत सारी रणनीतियों को नियोजित किया गया है। विभिन्न रणनीतियों के बीच सूप्रामॉलेक्युलर इंटरैक्शन सबसे काफी लुभावने और सम्मोहक रहे हैं। सूप्रामॉलेक्युलर इंटरैक्शन में मूल रूप से जटिल और कार्यात्मक सामग्रियों के निर्माण के लिए साधारण बिल्डिंग ब्लॉकों के गैर सहसंयोजक कॉम्प्लेक्स शामिल हैं। नैनोफाइबर्स को तैयार करने के लिए इलेक्ट्रोस्पिनिंग तकनीक की प्रयोज्यता के दायरे को चौड़ा करने के लिए, बहुलक / उभयसंवेदी (एम्फीफाइल) के बीच सूप्रामॉलेक्युलर इंटरैक्शन का एक मजबूत मार्ग है जो कठोर / अर्धकठोर बहुलक के लिए प्रस्तावित है, अन्यथा इनकी प्रयोज्यता इलेक्ट्रोस्पिनिंग तकनीक के लिए सीमित हैं। सबसे आम बहुलक उम्मीदवारों में से एक, जो सूप्रामॉलेक्युलर इंटरैक्शन के लिए एक घटक के रूप में उपयोग किया जाता है, वह है पॉली (4-विनाइल पाइरिडिन) (P4VP)। P4VP बहुलक के साइड चेन लटकन समूह कई कार्यात्मक अणुओं के साथ मेल कर सकते हैं, जैसे कि इलेक्ट्रोस्टैटिक, हाइड्रोजन बॉन्डिंग, समन्वय बंधन आदि के माध्यम से। इसलिए, सुपरमॉलेरिकल इंटरैक्शन की इंटरैक्शन शक्ति का प्रभाव रियोलॉजी और इलेक्ट्रोलस्पिनिबिलिटी पर समझना आवश्यक है। वर्तमान शोध कार्य में, P4VP जो विभिन्न उभयसंवेदी रासायनिक कार्यात्मक सिर समूहों के साथ विभिन्न मेलजोल के माध्यम से सूप्रामॉलेक्युलर कॉम्प्लेक्स बनाता, उधाहरण: डोड्साइलबेंजीनसल्फऑनिक एसिड (DBSA), 3-पेंटाड्साइलफेनोल (3-PDP) और Zn^{+2} डोड्साइलबेंजीनसल्फऑनिक एसिड लवण, का विस्तार में अध्ययन किया गया है। बहुलक के साथ इस तरह के उभयसंवेदी के साथ के मेलजोल के परिणामस्वरूप सूप्रामॉलेक्युलर कंघी बहुलक बनता है और उभयसंवेदी के झूलने वाले एल्काइल पूंछ गैर-ध्रुवीय मेलजोल से गुजरते हैं, जिसके परिणामस्वरूप बहुलक अन्तर्चैन संघ होते हैं। इस प्रकार, अलग-अलग इंटरैक्शन ताकत वाले उभयसंवेदी के कार्यात्मक सिर समूह भी इस तरह के बहुलक अन्तर्चैन संघों की स्थिरता का निर्धारण करते हैं, जो उभयसंवेदी के साथ झूलते गैर ध्रुवीय एल्काइल टाइलों द्वारा उभारा जाता है। यह फलस्वरूप रियोलॉजीकल गुणों और इलेक्ट्रोलस्पिनिबिलिटी को प्रभावित करता है। इसके अलावा, इस तरह के सूप्रामॉलेक्युलर कंघी बहुलक में स्वयं को पदानुक्रम

संरचनाओं में व्यवस्थित करने की प्रवृत्ति होती है, जो कि उभयसंवेदीयों के चयनात्मक निष्कासन से संभावित अनुप्रयोगों के लिए झरझरा / चैनल संरचनाओं का लाभ उठा सकते हैं।

इसके लिए, वर्तमान शोध कार्य में, P4VP और उभयसंवेदीयों के बीच अलग-अलग इंटरैक्शन ताकत के सूप्रामॉलेक्युलर कॉम्प्लेक्स को तैयार किया गया। P4VP का, 3-पेंटाड्साइलफेनोल (3-PDP) से मेलजोल हाइड्रोजन आबंध के माध्यम से, डोड्साइलबेंजीनसल्फऑनिक एसिड (DBSA) से मेलजोल आयनिक आबंध के माध्यम से जबकि, Zn^{+2} डोड्साइलबेंजीनसल्फऑनिक एसिड लवण ($Zn(DBSA)_2$) से मेलजोल समन्वय आबंध के माध्यम से होता है। एफटीआईआर द्वारा संबंधित इंटरैक्शन की पुष्टि की गई और कॉम्प्लेक्स सल्यूशन के गुण निर्धारित किए गए। हाइड्रोजन आबंध पर आधारित सूप्रामॉलेक्युलर कॉम्प्लेक्स इतने गतिशील पाए गए कि P4VP /PDP कॉम्प्लेक्स की वो इलेक्ट्रोलस्पिनिबिलिटी को ज़्यादा प्रभावित नहीं कर पाए। यह संभवतया सल्यूशन में हाइड्रोजन आबंधों की अस्थिर प्रकृति के कारण था, क्योंकि गठित भौतिक नेटवर्क का विश्राम समय बहुत ही कम था। P4VP /PDP कॉम्प्लेक्स के इन सूप्रामॉलेक्युलर कंघी बहुलक के इलेक्ट्रोस्पन नैनोफाइबर्स, SAXS और DSC विश्लेषण में अपनी विशिष्ट मेसोमोर्फिक संरचना का प्रदर्शन किया। इसके अलावा, पीडीपी को बहुलक के साथ उनकी कमजोर मेलजोल के कारण इलेक्ट्रोस्पन नैनोफाइबर्स से आसानी से हटाया जा सकता है, जिसके परिणामस्वरूप झरझरा नैनोफाइबर्स का निर्माण हो सकता है। जबकि, इसके विपरीत, P4VP (DBSA) / DMF कॉम्प्लेक्स सल्यूशन में आयनिक मेलजोल से 0.05 के कम मोलर अनुपात पर ही, विस्कोलास्टिक गुणों पर एक प्रमुख प्रभाव पाया गया। हाइड्रोजन आबंध की तुलना में आयनिक आबंध की मजबूत इंटरैक्शन ताकत के कारण P4VP / DBSA कॉम्प्लेक्स के लिए विसकॉसिटी में काफी वृद्धि पाई गयी। इसलिए, P4VP / DBSA से गठित नेटवर्क में अधिक स्थिर अन्तर्चैन संघों के कारण विश्राम समय बहुत अधिक होने की संभावना थी। P4VP (DBSA) / DMF कॉम्प्लेक्स सल्यूशन में 12% के ही बहुत कम सांद्राता पर ही इलेक्ट्रोस्पन हो सका जो अन्यथा केवल P4VP के मामले में 35% तक भी संभव नहीं हो पाया था। इसके अलावा, SAXS विश्लेषण से पता चला कि इलेक्ट्रोस्पन नैनोफाइबर्स ने बल्क फिल्म की तुलना में काफी बेहतर लैमेलर ऑर्डर पाया गया, जो कि P4VP श्रृंखलाओं के फाइबर अक्ष के साथ पसंदीदा अभिविन्यास द्वारा संभव हुआ। आयनिक इंटरैक्शन और गैर-ध्रुवीय साहचर्य इंटरैक्शन का महत्व, आगे इस तथ्य से स्पष्ट था कि P2VP / DBSA और P4VP / BSA जटिलों में रियोलॉजिकल गुण और

इलेक्ट्रोलस्पिनिबिलिटी दोनों ही उस हद तक बढ़े, जहां या तो आयनिक इंटरैक्शन कमजोर थे या गैर-ध्रुवीय एल्काइल पूंछ इंटरैक्शन अनुपस्थित थे। सभी कॉम्प्लेक्स जटिलों में, P4VP ($Zn(DBSA)_2$ / DMF जटिलों में 0.01 के कम मोलर अनुपात पर ही विस्कोलास्टिक गुण में काफ़ी वृद्धि हुई। इस तथ्य का मुख्य कारण, $Zn(DBSA)_2$ के अणु समन्वय आबंध के माध्यम से एक समय में कई 4VP इकाइयों को बांधने की क्षमता हैं , जो आगे चलकर एल्काइल पूंछों के गैर-ध्रुवीय अंतःक्रियाओं के माध्यम से इंटरचैन संघों को सक्षम करते हैं। इस तरह की श्रृंखलाओं के बीच पारस्परिक क्रियाओं के परिणामस्वरूप इन जटिल सल्यूशन के समृद्ध रियोलॉजिकल गुण होते हैं। P4VP / $Zn(DBSA))_2$ के उच्च मोलर अनुपात में जटिल सल्यूशन स्टिकी राउज़ और स्टिकी रेपटेशन मॉडल द्वारा वर्णित स्केलिंग कानूनों का पालन करते हुए पाए गए। इसके अलावा, विभिन्न साहचर्य संयोजन के मेलजोल की सार्वभौमिकता का इलेक्ट्रोलस्पिनिबिलिटी पर असर इस तथ्य से स्पष्ट किया जा सकता है कि पॉली (2-विनाइलपिरिडीन) (P2VP) /$Zn(DBSA)_2$ और P4VP/$Zn(BSA)_2$ के मामले में रियोलॉजिकल गुण और इलेक्ट्रोलस्पिनिबिलिटी में उतना सुधार नहीं पाया गया, क्यूंकी या तो समन्वय इंटरैक्शन कमजोर थे या गैर-ध्रुवीय एल्काइल पूंछ इंटरैक्शन अनुपस्थित थे। इस प्रकार, कुल मिलाकर, वर्तमान कार्य इलेक्ट्रोलस्पिनिबिलिटी में सुधार के लिए सूप्रामॉलेक्युलर इंटरैक्शन दृष्टिकोण पर एक व्यापक मौलिक अध्ययन के बारे मे रिपोर्ट करता है जो कई कठोर / अर्ध-कठोर बहुलक के लिए लागू हो सकता है। इसके अलावा, इस दृष्टिकोण को झरझरा / पोरस और कार्यात्मक इलेक्ट्रोस्पन नैनोफाइबर्स के उत्पादन के लिए भी उपयोग किया जा सकता है।

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LIST OF ABBREVIATIONS

P4VP	*Poly(4-vinylpyridine)*
3-PDP	*3-pentadecylphenol*
DMF	*Dimethylformamide*
NM	*Nitromethane*
DDA	*Dodecanoic acid*
DDO	*Dodecanol*
DBSA	*Dodecylbezene sufonic acid*
P2VP	*Poly(2-vinylpyridine)*
BSA	*Benzenesulfonic Acid*
ZnO	*Zinc oxide*
$Zn(DBSA)_2$	*Zn salt of dodecylbenzenesulfonic acid*
$Zn(BSA)_2$	*Zn salt of benzenesulfonic acid*
SEM	*Scanning Electron Microscopy*
SAXS	*Small Angle X-ray Scattering*
POM	*Polarized Optical Microscopy*
DSC	*Differential Scanning Calorimetry*
PVA	*Poly(vinyl alcohol)*
PEO	*Poly(ethylene oxide)*
HASE	*Hydrophobically modified alkali-soluble emulsion*
BiOH	*4,4'-biphenol*
HBCA	*4-hydroxy-4'-biphenylcarboxylic acid*
HA	*Hylaruonic acid*
CS	*Chitosan*
PVC	*Poly(vinyl chloride)*
PAA	*Poly(acrylic acid)*
PVPh	*Poly(vinylphenol)*
PVP	*Poly(vinylpyrrolidone)*
PMMA	*Poly(meth methyl acrylate)*
POSS	*Polyhedral oligomeric silsesquioxane*

$ZnCl_2$	*Zinc Chloride*
PAN	*Poly(acrylonitrile)*
CDs	*Cyclodextrins*
MβCD	*Methyl-β-cyclodextrin*
AFM	*Atomic Force Microscopy*
HABA	*2-(4'-hydroxy- phenylazo)benzoic acid*
KCl	*Potassium Chloride*
LVER	*Linear Viscoelastic Region*
BET	*Brunner-Emmet-Teller*
FTIR	*Fourier-Transform Infrared Spectroscopy*
TIPS	*Thermal induced phase separation*
DC	*Direct Current*

LIST OF SYMBOLS

η_o	*Zero shear viscosity*
η_s	*Solvent viscsoity*
η_{sp}	*Specific viscosity*
C^*	*Onset of semidilute unentangled regime*
C_e	*Onset of semidilute entangled regime*
C_D	*Onset of concentrated regime*
$[\eta]$	*Intrinsic Viscosity*
K and α	*Mark-Houwink-Sakurada constants*
N_a	*Avogadro number*
R_g	*Radius of gyration*
M_c	*Critical entanglement molecular weight*
M_w	*Weight average molecular weight*
R_0^2	*Mean square end to end distance at zero concentration*
R_θ^2	*Unperturbed dimensions of the polymer coil*
ρ	*Density of the neat polymer*
R	*Ideal gas constant*
T	*Temperature*
G_N^0	*Plateau modulus*
N_e	*Number entanglements per chain*
Mn	*Number average molecular weight*
C_{bf}	*Concentration of onset of beaded fibers formation*
C_f	*Concentration of onset of uniform fibers formation*
G^*	*Complex Modulus*
G'	*Storage/Elastic Modulus*
G''	*Viscous/Loss Modulus*
γ	*Shear Strain*
δ	*Phase shift angle*
τ	*Shear stress*

$\boldsymbol{F_{tens}}$	*Tension Force*
$\boldsymbol{F_G}$	*Gravitational Force*