

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 ($\text{Zn}(\text{DBSA})_2$), 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 ($\text{Zn}(\text{DBSA})_2$) 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 benzenesulfonic 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.