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Coacervation in Symmetric Mixtures of Oppositely Charged Rod-like Polyelectrolytes RAJEEV KUMAR, GLENN FREDRICKSON, Materials Research Lab, UCSB, CA — Phase separation in the salt-free symmetric mixtures of oppositely charged rodlike polyelectrolytes is studied using quasi-analytical calculations. Stability analyses for the isotropic-isotropic and the isotropic-nematic phase transitions in the symmetric mixtures are carried out. It is shown that electrostatics favor nematic ordering. Also, the coexistence curves for the symmetric mixtures are computed, and the effects of the linear charge density and the electrostatic interaction strength on the phase boundaries are studied. It is found that the counterions are uniformly distributed in the coexisting phases for low electrostatic interaction strengths characterized by the linear charge density of the polyelectrolytes and the Bjerrum's length. However, the counterions also phase separate along with the rodlike polyelectrolytes with an increase in the electrostatic interaction strength. It is shown that the number density of the counterions is higher in the concentrated (or coacervate) phase than in the dilute (or supernatant) phase. In contrast to the rodlike mixtures, flexible polyelectrolyte mixtures can undergo only isotropic-isotropic phase separation. A comparison of the coexistence curves for the weakly charged rodlike with the flexible polyelectrolyte mixtures reveals that the electrostatic driving force for the isotropic-isotropic phase separation is stronger in the flexible mixtures.

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