Chemical demulsification is the most widely used method for breaking water-in-diluted bitumen emulsions in oil sands processing. In this paper, the properties and the performance of six series of ethylene oxide (EO) - propylene oxide (PO) block copolymer demulsifiers from two families were investigated. The demulsifiers were characterized by their relative solubility number (RSN), EO content, PO content and molecular weight (MW). The results showed that the performance of demulsifiers was correlated to starting base compound, EO content, PO content, RSN, MW, degree of crosslinking among EO-PO demulsifiers, interfacial tension (IFT), yield stress of underflow, and bitumen loss. Demulsifiers with a higher molecular weight and more EO-PO branching had higher dehydration efficiency when EO content was varied from 0 to 40% at constant PO content. An increase in MW by crosslinking EO-PO copolymers improved the dehydration efficiency. In this work, an appropriate rheological method was developed to correlate properties of demulsifiers with properties of underflow. The yield stress of the underflow, which included settled solids, water, and rag layer increased with increasing RSN value and dosage of demulsifier. At high dosages, the yield stress values were high due to the increased number of aggregates, which in turn restricted underflow. An increase in the RSN value of demulsifiers led to more bitumen loss to the underflow, which increased the size of the aggregates present in the underflow, resulting in increased immobility and constriction, and higher yield stress.