

Stabilization of Submicron Metal Oxide Particles in Aqueous Media

by
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Abstract

An investigation into the parameters that define a good anchor block for a copolymer steric stabilizer was performed. The study focused on the effects of different functional groups on the adsorption properties of polymers. In addition, the effect of chain architecture as well as the impact of a hydrophobic end-group on polymer adsorption properties was determined. To complement the adsorption studies, a streaming potential instrument was built for use in measuring the adsorbed layer thickness of nonionic polymers on SiO_2 . The research concluded with an examination of the effect of thermally induced insolubility on adsorption of a hydrogen-bonding polymer.

Functional group effects were studied by measuring the adsorption isotherms of poly(2-ethyl-2-oxazoline), PEOX, poly(ethylene oxide), PEO, poly(vinyl alcohol), PVOH, and poly(ethylene imine), PEI, which was modified such that a 1,3-butanediol substituent replaced its imine hydrogens, on SiO_2 , TiO_2 , and Al_2O_3 . PEOX and PEO, relatively basic polymers compared to PVOH were observed to adsorb only on the most acidic metal oxide, SiO_2 . PVOH, however, was observed to adsorb on all three metal oxides, but to a lesser degree on SiO_2 as compared to the more basic PEOX and PEO. These initial results were indicative of hydrogen-bonding mechanisms, a form of acid-base interaction.

The most significant observation in the adsorption studies was that the linear hydroxyl modified PEI materials and their dendritic analogs adsorb on the metal oxides both above and below the i.e.p. This indicates that both electrostatic and hydrogen-bonding mechanisms are driving the adsorption. The dendritic polymers, particularly a 4th generation dendrimer based on diaminopropane with a molecular weight of 16,640 g/mol

adsorbed at a higher level when compared to the 41.3K g/mol PVOH and 30K g/mol PEOX. In addition to the dual adsorption mechanism, it was determined that the dendritic architecture appears to facilitate adsorption, as does the presence of the hydrophobic endgroup. The level of adsorption for all of the hydroxyl containing linear PEI and dendritic materials on the three metal oxides was high enough for them to be considered as anchor blocks in a copolymer steric stabilizer.

The streaming potential instrument used to measure the adsorbed layer thickness on SiO_2 . Adsorbed layer thickness of PEOX $M_w = 10\text{K}$ and 30K g/mol were measured at approximately 1nm and 4.4 nm, respectively. In the case of the PEOX $M_w = 30\text{K}$ g/mol homopolymer, the measured layer thickness was higher than that for a 23K g/mol PEO homopolymer. The degree of polymerization of the PEO is approximately 525, while for the PEOX it was only 300. This result was not expected.

Finally, adsorption of PEOX was studied at the cloud point to determine whether insolubility could promote adsorption, while hydrogen-bonding, the room temperature driving force for adsorption, would decrease. Adsorption isotherm measurements were performed at 72°C and 75°C , as the cloud point of the 30K PEOX was determined to be 73°C . It was apparent that the adsorption decreased as temperature increased, indicating that without hydrogen bonding, thermally induced insolubility does not drive adsorption.