



## RADIATION STABILISATION of HYPERSWOLLEN POLYMER

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If sodium dodecyl sulphate, SDS, is added to a latex of poly(vinyl acetate), PVAc in water, to give an overall SDS concentration greater than 4.5 mM, the polymer latex particles swell reversibly to a final volume of the particles up to fifty times their original volume. 96% of the increase is due to water carried in with the SDS. The swelling is attributed to the formation of polymer micelle complexes (PMCs) along the polymer chains. The charges on these PMCs repel, thus expanding the particles. Entanglement of higher molecular weight chains inhibit swelling beyond an equilibrium value.<sup>1</sup>

If, however, the swollen particles are irradiated in a gamma source and then dialysed, they shrink only slightly to approx. forty times the original volume indicating that the charges are attached irreversibly to the PVAc chains. The maximum effect is observed at 12 kGy (dose rate 0.12 Gy/s) and at a molecular ratio PVAc : SDS of 12; both of which indicate that grafting has occurred.

We believe that the radical products from the radiolysis of water abstract hydrogen from the methylenic groups of the surfactant tail and from the VAc units of the polymer. The resulting surfactant radicals react with those on the polymer chains giving a strong co-valent bond. On dilution or dialysis the excess surfactant is removed leaving the permanently grafted molecules still attached to the chains. The chains thus have a structure similar to an entangled polyelectrolyte and the repulsion between the charges on the grafted surfactant molecules keeps the particles expanded. If a salt solution is added, the repulsions are reduced by ionic electrostatic shielding and the particles shrink accordingly until a salt concentration is reached at which coagulation occurs.

These microgels are novel materials and we have been investigating their potential for new and useful purposes. The stabilised latices show a remarkable increase in colloidal stability towards coagulation in sodium chloride solution. The stabilised particles do not coagulate in salt solution 400 times as concentrated as that in which as-prepared unstabilised latices coagulate.

PVAc	initial	<-[SDS]->	final	[NaCl] <sub>coag</sub>
330 ppm	0 mM	after dialysis	0 mM	0.006 M
330 ppm	20 mM	dialysed	0 mM	0.022 M
1500 ppm	20 mM	diluted 4x	5 mM	0.8 M
330 ppm	20 mM	irrad'd+dialy	0 mM	1.8 M

In 2% VAc monomer / 20 mM SDS solution the nonstabilised expanded particles contract as the PMCs are displaced by monomer but stabilised particles remain the same size. This suggests that their use as an expanded seed for further polymerisation could have advantages.

These are examples of the unusual properties we have found in working on these systems and suggest additional novel uses. We are interested in cooperating on different practical applications of the reversible super-swelling and of the stabilised swollen particles.

REF Hidi, P.; Napper, D.H.; Sangster, D.F. *Macromolecules* 1995, 28, 6042