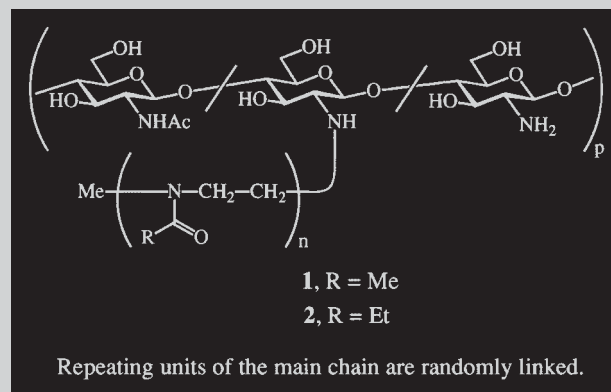


Full Paper: The molecular shapes and the sizes of structures formed by chitin derivatives with monodisperse poly(2-alkyl-2-oxazoline) side chains were investigated using atomic force microscopy (AFM), cryo-transmission electron microscopy (cryo-TEM), and small-angle neutron scattering (SANS) analyses. A ring structure with an outside diameter of 45–60 nm and a cross-sectional diameter of 10–18 nm was observed in the AFM image for chitin-*graft*-poly(2-methyl-2-oxazoline) **1d** (*DP* of the side chain, 8.5; [side chain]/[glucosamine unit], 0.53). From the cryo-TEM observation of the graft copolymer **1d** in 0.5 wt.-% D₂O solution, an average diameter of 40 nm for the particles was determined, with a narrow size distribution. SANS measurements of the 0.5 wt.-% D₂O solution of **1d** revealed that the outside diameter of the particles and the cross-sectional diameter were 57 nm and 8 nm, respectively. The absolute weight average molecular weight of **1d** was determined to be 5.4×10^5 by static light scattering. From these results it was concluded that **1d** can form a unimolecular ring structure in aqueous solution. However, graft copolymers with fewer side chains (**1c**; [side chain]/[glucosamine unit], 0.30) and with more side chains (**1e**; [side chain]/[glucosamine unit], 0.96) did not form rings but instead formed monodisperse unimolecular spherical particles of diameters of 28–36 nm by AFM. A graft copolymer **1f** with relatively long side chains (*DP* of side chain, 19.6; [side chain]/[glucosamine unit], 1.00) was also observed as a spherical particle by AFM (diameter: 30–40 nm by AFM; 40 nm by SANS). On the other hand, an intermolecular aggregate formation (diameter of the aggregate: 36–143 nm) was observed for graft copolymers **1a** and **1b** having short side chains (*DP* of side

chains, 5.6; [side chain]/[glucosamine unit], 0.35 and 0.48, respectively), with a spherical molecular particle of diameter 36 nm by the AFM analysis. Chitin-*graft*-poly(2-ethyl-2-oxazoline) (**2**) (*DP* of side chains, 21.7; [side chain]/[glucosamine unit], 0.95) generated larger aggregates of diameter 100–400 nm by AFM. The complexation behavior of graft copolymer **1d** with magnesium 8-anilino-1-naphthalenesulfonate (ANS) and with *N*-phenyl-1-naphthylamine (PNA) was also examined by fluorescence measurement in an aqueous solution. It was found that graft copolymer **1d** complexed with both ANS and PNA, and the binding constants were calculated to be $7.5 \times 10^4 \text{ M}^{-1}$ and $5.3 \times 10^4 \text{ M}^{-1}$, respectively.



Chemical structure of chitin-*graft*-poly(2-alkyl-2-oxazoline).

Nano-Scale Molecular Shapes of Water-Soluble Chitin Derivatives Having Monodisperse Poly(2-alkyl-2-oxazoline) Side Chains

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