In synthetic polymer science, useful information can be obtained by using an assumed mechanism to predict the molecular weight distribution (MWD), and then comparing with qualitative and quantitative trends in experiment (e.g. 1) and general inferences (e.g. 2). Starch is a highly branched polymer of glucose, with two forms: amylopectin, comprising many short-chain branches forming crystalline lamellae, and amylose, which has only a few long-chain branches. MWDs of individual branches (the chain-length distribution, CLD) in starch-synthesizing organisms is controlled by complex biosynthetic pathways involving numerous enzymes. A mathematical model for the time evolution of starch CLD is developed assuming that an individual branch grows under the control of the three types of enzymes: the synthases (which add glucose units—propagation), the branching enzymes (which are restricted to operating on portions of chain greater than certain minimal degrees of polymerization) and the debranching enzymes (which create and remove branches respectively). The CLD is then dictated by only two parameters: the ratios of the rate of branching to that of propagation, and of debranching to propagation. Solution of the time evolution equations based on the eigenvalues of the corresponding matrix shows that amylopectin branches in starch-accumulating plants are confined to a very restricted range of rates; mutations leading to enzymatic rate parameters outside this region would be inferior variants. This prediction is supported by fitting extensive data for varying types of such plants (as exemplified in Fig. 1). Moreover, the model predicts the presence of a small shoulder at low degrees of polymerization, an effect which had never been noticed but in fact can be distinguished in a wide range of literature data. This, plus good agreement between observed and the model for a wide range of plants (including mutants) suggests new methods, limitations and targets for plant engineering aiming for changing CLDs (e.g. to produce starches with long branches, which has nutritional advantages for slow digestion).

Fig. 1. Experimental and fitted CLD for wheat (experimental data from Castro et al. 3). Arrow indicates predicted shoulder.

3 Castro, J.V.; Dumas, C.; Chiou, H.; Fitzgerald, M.A.; Gilbert, R.G. Biomacromolecules 2005, 6, 2248.