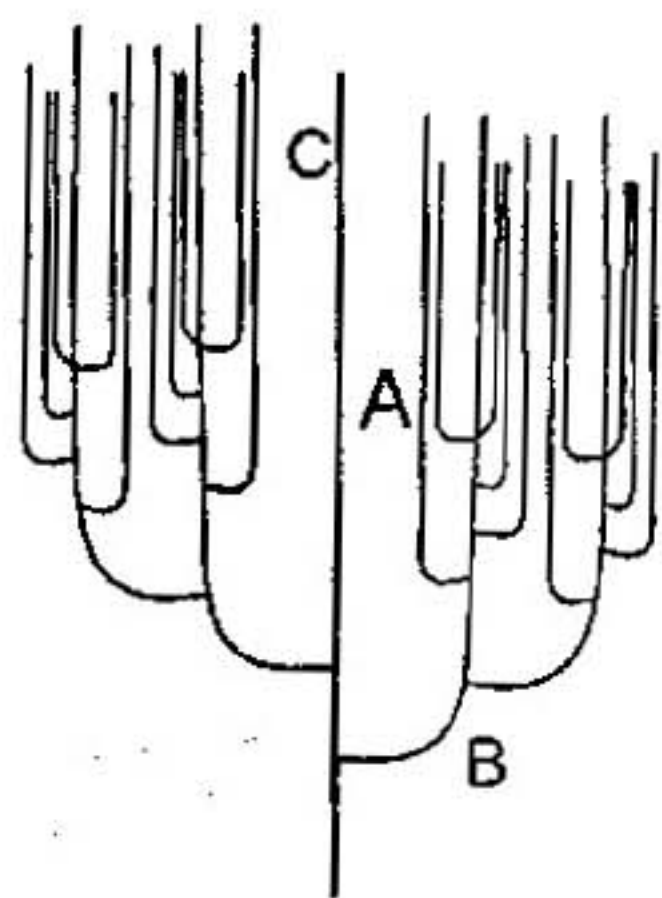


Characterization and Modification of Natural Hydrocolloids with the Techniques of Synthetic Polymer Colloids

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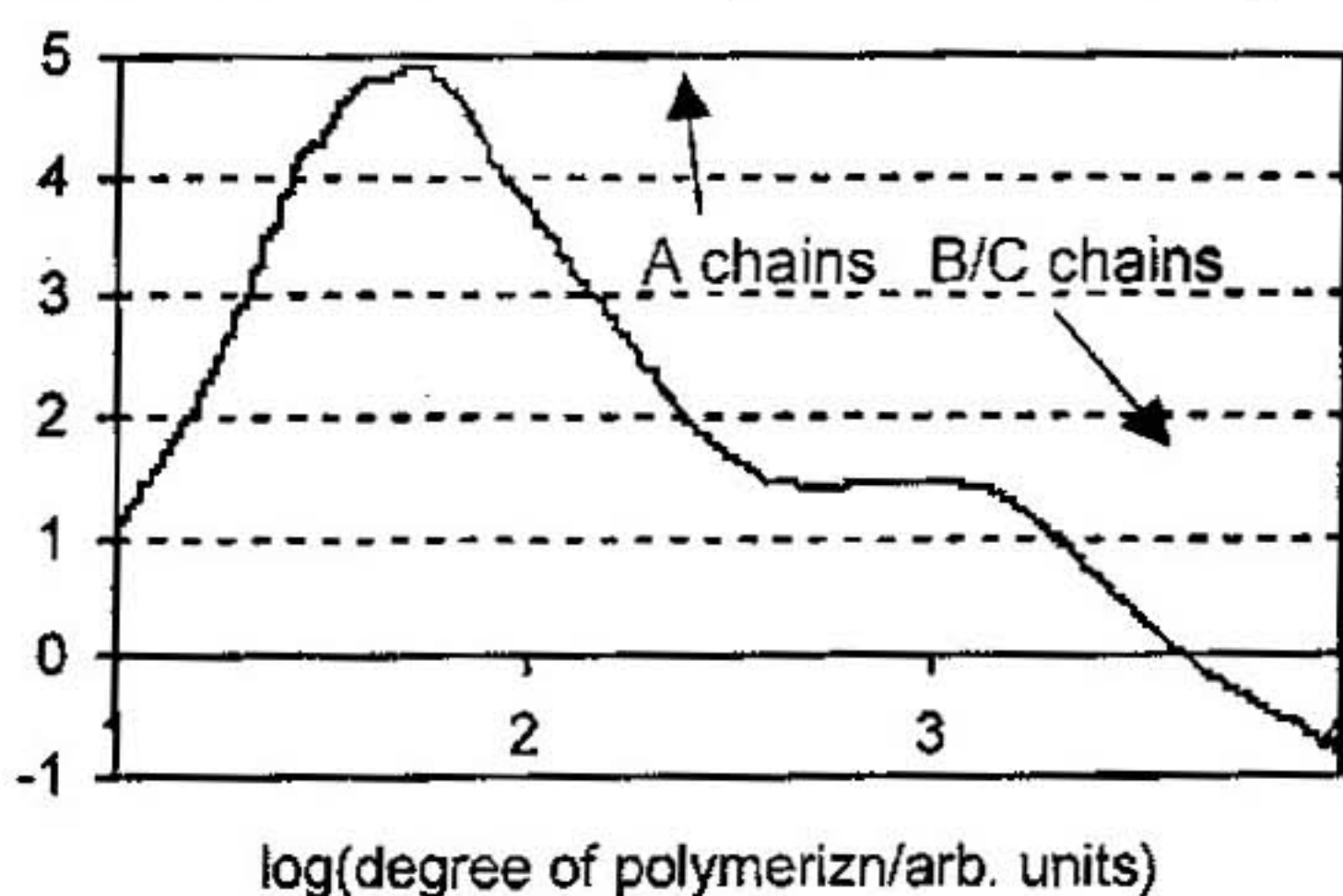
Starch is a natural hydrocolloid, and is a polymer of glucose. It comprises two forms: amylose, which is largely linear with a few long branches, and amylopectin, which is highly branched and comprises so-called A, B and C chains. The relative amounts of amylose and amylopectin, and the branching structure of each, depend not only on the plant species but also on the plant variety (genotype) and environmental and agronomic conditions. This molecular architecture also affects many of the eating and processing properties.

The molecular weight distribution of these chains is governed by the underlying enzymatic processes involved in starch synthesis. An approach that has been used for this purpose is to snip all branch points with a debranching enzyme and examine the result using GPC. However, such data have never been quantitatively interpreted.

A method has been developed for quantitative interpretation of MWDs in *synthetic* polymer colloids (see Gilbert, R. G. *Emulsion Polymerization: A Mechanistic Approach*; Academic: London, 1995). An example is if the chain growth and termination rates are both proportional to monomer concentration, in which case one has:

$$\ln(\text{number MWD}) = \ln \frac{\text{GPC distribution}}{N^2} = -\frac{k_{\text{term}}}{k_{\text{growth}}} N \quad (1)$$

where N is the degree of polymerization, and k_{term} and k_{growth} are the rate coefficients for chain termination (e.g. by transfer to monomer) and growth (propagation). We have applied this methodology to rice starch. A variant of the preparation procedure was developed, debranching performed with isoamylase (Lisle, A. J.; Martin, M.; Fitzgerald, M. A. *Cereal Chem.* 2000, 77, 627), and a GPC protocol



developed which gave a good GPC distribution (see figure) including resolution of A and B/C chains. Data interpretation using eq 1 requires absolute, not relative, molecular weights, but neither standards nor Mark-Houwink parameters are available for debranched amylopectin. This was overcome by obtaining the MWD using asymmetric-flow field-flow fractionation with LALS detection. The results show peaks corresponding to A and B chains (the latter with some C chains also present), and a high molecular weight peak that is probably due to agglomerates. The number MWDs for both A and B/C

peaks so obtained appear to show the linearity predicted by eq 1, with different slopes for the different types of chains. This suggests that the rates of the enzymatic processes for both chain-growth and chain-stopping processes are proportional to the concentration of glucose monomer. This technique has considerable potential for quantitative mechanistic interpretation of the enzymatic processes involved in the formation of starch.

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