

THE COMBINED USE OF LAGUERRE TRANSFORMS AND NUMERICAL
EVALUATION OF GENERATING FUNCTIONS FOR COMPUTING POLYMER
CHAIN LENGTH DISTRIBUTIONS

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Evaluation of probability generating functions (PGF) of polymer chain-length distributions (CLD), often only by numerical means, provides an efficient and accurate method for predicting average chain-lengths, even in more difficult cases such as non-linear free radical polymerizations.

Weeks' method for Laplace transform inversion, based on an expansion in orthogonal Laguerre functions, has already been previously used by other research groups for recovering the CLD in combination with numerical evaluation of PGF for polymer CLD.

We present in this work an improved method eliminating all un-needed references to the continuous chain length approximation. Remarkably accurate results can be achieved with only a few tens of evaluations of PGF for most kinds of CLDs not presenting sharp peaks (e.g., excluding Poisson distributions and similar).

The presence of chain-length dependent rate parameters as found in polycondensations with ring formation or because of termination reactions in free-radical polymerization gives rise to additional mathematical difficulties in the calculation of the PGF of polymer CLD, as the population balance equations in Laplace domain now include terms with complex contour integrals. We present algorithms for dealing with these situations, considering as examples ring formation in linear polycondensations and chain-length dependent rate of termination in free-radical polymerization.

The alternative approach consisting in trying to compute the sequence of Laguerre expansion coefficients in the real chain-length domain is finally compared.