27g Model Based Design of Structured Polymers Using the Reverse Design Approach

Vipasha Soni, Jens Abildskov, Gunnar E. Jonsson, Rafiqul Gani, Nikos Ch. Karayiannis, and Vlasis Mavrantzas

In separation processes involving polymeric membranes one is interested in the design of new structured polymers that can guarantee the desired degree of separation for the given mixture under study. Two methods are usually followed to address such a design problem: in the first, a trial-and-error procedure is followed where different candidate polymers are tested; the design variables being a set of operational parameters like temperature, pressure and composition, all affecting the membrane permeability and mass flux. In the second, which is the one followed in this work, a reverse approach is followed according to which one is interested in the design of the polymer with that particular microscopic structure that would optimally match the specified permeability separation standards.

Key in the new method is the assumption that the permeability properties of a polymeric system are intimately related to its microscopic structure (i.e., monomer composition) and/or chain conformation. The design procedure in this case involves fixing the desired degree of separation for the given mixture and then selecting the optimal polymer based on a property model. Developing such property models requires information on how properties like density, diffusivity, solubility, etc., vary as a function of polymer structure and architecture (e.g., length and degree of branching). Acquiring this information from computer simulation approaches sound particularly appealing since true experiments are usually time consuming and expensive.

In this work, results will be presented for the case where one is interested in the structural, volumetric and dynamic properties of a rather simple polymer, that of polyethylene, as a function of its molecular architecture, that is of branch length and branch frequency. Sufficient data about the equilibrium radius of gyration of linear and branched PE, the longest relaxation time, and the chain center-of-mass self-diffusion coefficient have been obtained in this case from a computer simulation approach based on a state-of-the-art Monte Carlo simulation algorithm (to obtain the thermodynamic and conformational properties of the polymer) followed by a long simulation with a multiple-time-step molecular dynamics method to get the dynamic properties (spectrum of relaxation times, zero shear rate viscosity and chain diffusivity). By analyzing these data using well established group contribution methods, closed-form analytical expressions are developed capable of relating these properties to features of molecular structure and conformation of the polymer. For the case of PE considered here, these include the molecular length (number of carbon atoms) of the main chain backbone, the molecular length of the branches and the spacing between successive branch points along the chain (branch frequency). Representative results from this analysis followed by examples of reverse calculations (and how they compare to simulation data that were masked in the group contribution analysis step) that fully validate the proposed methodology will be presented and discussed in detail. In the future, the method will be extended to developing similar property models for other polymers, such as polypropylene, cis-1,4 polybutadiene, polyisobutelene, etc.