

INSPIRATIONS FOR EO POLYMER DESIGN GAINED FROM MODELING OF CHROMOPHORE POLING BY LANGEVIN DYNAMICS

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Over last two decades there is a stable interest to make use of organic molecular materials in a wide variety of NLO applications [1]. One of the possibilities to create a material for these applications, like EO modulators, is polymer with dispersed NLO active chromophores. In general there are two types of such systems – “host/guest” systems with NLO active chromophores admixed in polymer matrix and so called “grafted” polymers where chromophores are covalently bounded to polymer. To act in an NLO material chromophores must be acentrically aligned, what is generally achieved by applying an electric poling field. The NLO efficiency depends on dipole moment, molecular hyperpolarizabilities, concentration of the chromophores and external poling field strength. Calculating, from first principles, the extent of the alignment and via this NLO efficiency has proven to be challenging. One approach to solve this problem is pure analytic statistical mechanics treatment [2], what could be enhanced by Monte Carlo (MC) statistical mechanical modeling[3,4]. The chromophore molecules usually have been treated as point dipoles embedded in some kind of realistic molecular shape – prolate spheroid. From our point of view, at short intermolecular distances model of interacting point dipoles is not appropriate representation for electrostatic interactions of chromophores. Another disadvantage of these MC based statistical mechanical methods is impossibility to get some insight in poling (relaxation) dynamics. Fully atomistic molecular modeling with classical force field molecular dynamic (MD) methods allows observing the time evolution of a system [5]. Unfortunately, in case when host and chromophores are represented at atomistic level, MD approach requires huge amount of computations. One of the solutions is to reproduce the motion of the molecules of interest (chromophores) using Langevin dynamics (LD). This method simulates the effect of molecular collisions and the resulting dissipation of energy that occur in real host, without explicitly including host molecules. In this contribution, we would like to present results of our LD simulations of the model systems. In the case of modeling “host/guest” NLO polymers chromophores have rotational and translational freedom. Restricting translational movement of chromophores allows us to model “grafted” NLO polymers. Chromophore load, dipole moment and poling field impact on extent of alignment and poling / relaxation dynamics of model systems obtained by LD simulations will be presented. In general, both prototypical systems according to our simulations behave similar, except formation of dipolar chromophore chains in case of “host/guest” model (see fig.). Formation of such chains has positive effect on polar order stability and in some cases could yield in “ferroelectric” behavior of polymer. On a basis of these results we would like to come forward with some inspirations for EO polymer design.

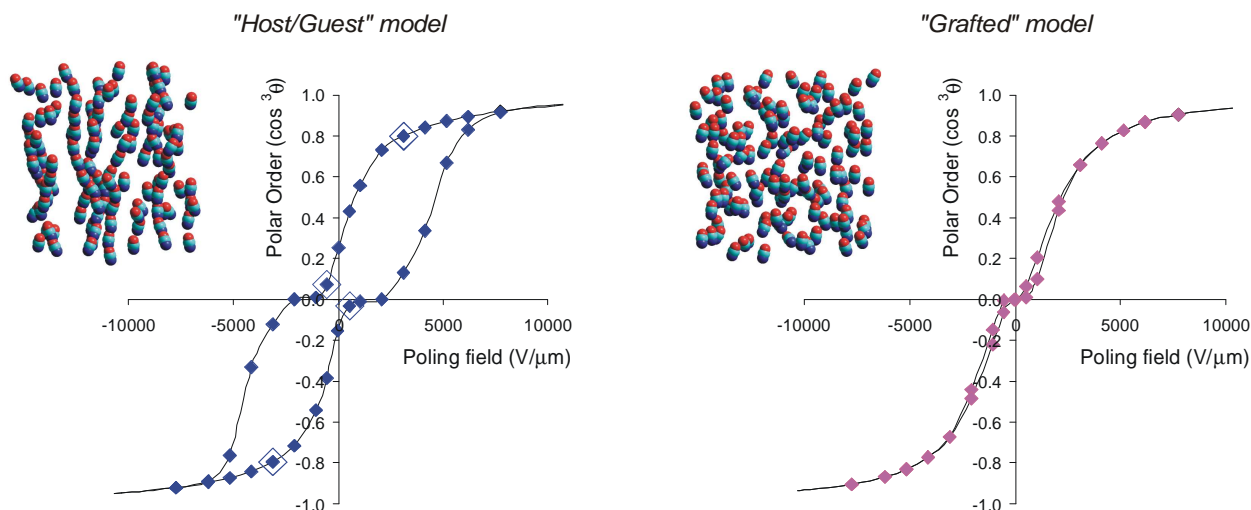


Figure 1. LD simulation of polarization:

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