

# Effect of Stacking Interactions and Conformation on Polymer Polarizability

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The Long-Range Corrected density functionals (LC-DF)[1] represent dynamical polarizabilities of medium-sized organic and metal-organic compounds with very good accuracy.[4,5] The functional with 100% of Hartree–Fock (HF) exchange at long-range, LC-BLYP[2], performs best for aromatic compounds and CAM-B3LYP[3] for saturated compounds. These excellent benchmark results motivated us to apply LC-DF's to study optical properties of polymers. If repeat unit models are corrected for end-effects, refractive index and Abbe number of large number of non-conjugated polymers is represented with very good accuracy, for example, for polystyrene (PS), poly(methyl methacrylate) and CYTOP wavelength-dependent refractive indices exceptionally good agreement (rmsd within 0.004).[6] The latter results, as well as some tendency to overestimate refractive index in polymers rich in large aromatic moieties, prompted us to study how stacking between aromatic moieties affects polarizability.[7] We study diads (dimers) with aromatic substituents containing six to fourteen pi electrons. The stacking of aromatic substituents in meso-tg, racemo-tg and racemo-tt conformers causes polarizability decrease relative to conformers, in which substituents are separated, for example, meso-tg. The polarizability reduction is more pronounced in larger aromatic systems. In PS, the experiment [8] and simulations [9] suggest that meso-tg, racemo-tg and racemo-tt diads are favored, in which no stacking of phenylenes is observed. Consequently, the refractive index based on (simulated and experimental) diad populations, is practically the same as the monomer-based refractive index, with both values in excellent agreement with the experimental value of 1.592.[6] We extend this analysis to, among others, poly(ethylene terephthalate), for which a nonbonded dimer model similar to that of parallel displaced benzene dimer predicts refractive index in excellent agreement with experiment. From the knowledge of polarizability changes upon stacking, and conformer population, estimation of this effect in condensed systems appears possible.

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