A Combined Density Functional and Monte Carlo Study of Polycarbonate

R. O. Jones and P. Ballone[*]
Institut für Festkörperforschung, Forschungszentrum Jülich,
D-52425 Jülich, Germany

ABSTRACT

Density functional computations have been performed to investigate the structure, potential energy surface and reactivity for organic systems closely related to bisphenol-A-polycarbonate (BPA-PC). The results provide the basis for the construction of two different empirical models, the first extending the atomistic simulations into the mesoscopic range ($10^4 - 10^5$ atoms and $0.01 - 0.1$ $\mu$s), the second providing an idealized description of polymerization in BPA-PC. The combination of models and computational techniques focusing on different length and time scales provides a route to determine mechanical and thermal properties of materials without experimental input.

INTRODUCTION

Polymer science was one of the first fields where the importance of multi-scale relations and phenomena was recognized, providing the motivation for renormalization group approaches [1]. Standard applications of these methods to polymers assume that their behavior arises from the cooperative interaction of different length and time scales, while the details of the atomic and chemical structure determine some collective parameters, but are otherwise unimportant. The vast literature on these methods testifies to their power and success. Nevertheless, we are increasingly confronted with problems that require a detailed description of the structure, dynamics and chemical properties on different scales of time and length, so that we can investigate all those properties that are not universal. We shall show here that different models and computational methods can be combined to provide a detailed description of polymers, using bisphenol A polycarbonate (BPA-PC) as an example.

The polycarbonate family includes materials with outstanding mechanical, optical and thermal properties, and a wide range of applications. Although production and processing of polycarbonates have been carried out on an industrial scale for several decades, there remain important questions concerning the relation between the macroscopic behavior and the structure and chemistry at the atomistic level that require a multi-approach investigation. A detailed understanding of the relationship between structure and properties should provide the basis for the development of new variants of these materials.

Our strategy has been to study the atomistic behavior by parameter-free density functional (DF) calculations, which provide the basis for developing empirical models that extend the size and time scales into the mesoscopic domain ($10^4 - 10^5$ atoms and $0.01 - 0.1$ $\mu$s). This allows the investigation of inhomogeneous systems, and of mechanical and thermal properties. Moreover, the DF results provide both the inspiration and the input parameters for more idealized models, with which we have studied the equilibrium polymerization of polycarbonates.
Density functional theory [2] provides the microscopic basis for our approach. Progressive improvements in the exchange-correlation functionals [3], efficient numerical implementations, and vastly improved computer facilities have all contributed to its acceptance as a method with predictive capability for calculating total energies, ground state structures and low energy dynamical properties for a wide variety of systems. Applications to polymers are among the most recent, but the results to date are very encouraging.

The analysis of the inter-atomic interactions in BPA-PC began with a series of computations for molecular fragments (carbonic acid, benzene, phenol, mono- and diphenyl carbonate, see Fig. 1), for a short BPA-PC segment comprising two carbonate groups linked by a propylidene vertex (DPBC), and for the cyclic dimer and tetramer [4]. Experimental structural data are available for most of these.

The agreement between computed and measured intramolecular bonding parameters is very satisfactory, with discrepancies (~ 1%) that are near the limit of the experimental resolution. Harmonic vibrational frequencies are also predicted with remarkable accuracy, although in this case discrepancies (up to 3 – 4% in the harmonic frequencies) are significantly larger than the experimental error bars. Complex intramolecular interactions occur in the cyclic dimer and tetramer, where there is a balance between local bond formation and the geometrical constraint of forming a ring. The constraint is more severe for the dimer than for the tetramer, resulting in a strained ground state structure for the dimer (with the unusual cis-trans conformation for its carbonate groups), while it is remarkably strain free for the tetramer, with interatomic distances and angles close to those found for the molecular fragments. Both molecules crystallize in rather simple crystal forms, and the DF ground state structures agree very well with the experimental X-ray diffraction results.

As expected, DF is less successful in describing the long range attractive forces that bind BPA-PC molecules, since dispersion interactions are not included in standard DF approximations. As a result, the cohesion of the molecular crystals is underestimated, with corresponding overestimates in the equilibrium volumes [5]. The agreement between computed and experimental data can,
however, be improved by the addition of dispersion forces, modeled by the attractive tail of the Lennard-Jones potential.

**CRYSTALLINE ANALOGS OF POLYCARBONATE**

The mechanical toughness of BPA-PC is related to its ability to transfer and dissipate energy, while avoiding the accumulation of local excitations that could cause damage. The atomistic mechanism responsible has not been identified unambiguously, although several related to the intermolecular interactions have been suggested. The DPBC molecule mentioned above is interesting in this context, because it crystallizes in two structures that differ mainly in the degree of molecular packing. The more stable form at low temperature [6] (Fig. 2, left) has a unit cell with two DPBC molecules (118 atoms), and the second polymorph (Fig. 2, right) has a unit cell with four DPBC molecules (236 atoms) [7]. The molecules are arranged in both cases in a head-to-tail geometry that mimics the structure of long chains in amorphous BPA-PC.

The dynamical feature that distinguish these two forms is the \( \pi \)-flip of the phenylene rings, which occurs readily in the “mobile” form with lower density, while it is hindered in the “immobile”, low temperature form. Crystals of DPBC then offer an opportunity for investigating the relation between intermolecular packing and dynamics, unaffected by the fluctuations and disorder that characterize amorphous polymers.

The DF computations [8] reproduce very well the experimental atomic positions, and allow us to simulate the \( \pi \)-flip of phenylene rings by constraining the torsional angles that define the relative orientation of the benzene and carbonate planes. All other degrees of freedom are relaxed by quenched molecular dynamics (MD) [9]. Preliminary computations have shown that the phenylene rings rotate freely in the isolated DPBC molecules, implying that any barrier found in the crystal phases comes from inter-molecular interactions. In agreement with experiment, we found that the lowest energy barrier for the phenylene \( \pi \)-flip in the crystal occurs in the mobile form, and is associated with the motion of the inner ring of DPBC. The calculated barrier (7.7 kcal/mol) is close to

![Figure 2: Structures of crystalline forms of DPBC. Left: “immobile” (118 atoms per unit cell), right: “mobile” (236 atoms per unit cell).](image)
to the experimental estimates (8 – 10.4 kcal/mol). The π-flip in the immobile form must overcome a barrier of 16.3 kcal/mol, due to short range repulsions between the ring that rotates and one on a neighboring molecule. The barrier for the rotation of the carbonyl group is large (19 kcal/mol) and arises from intra-molecular interactions. The rotations of the methyl groups are little affected by the molecular packing, and are relatively low (3.4 kcal/mol) in all cases that we analyzed.

These results show that DF calculations are able to predict accurately energy barriers associated with short range inter-molecular interactions, and they allow us to identify the mechanism (rotation of the inner ring) responsible for a prominent dynamical feature of DPBC. Moreover, they provide much quantitative detail on the complex potential energy surface of condensed polycarbonates. This last feature, in particular, is used for the construction of simplified models.

**EMPIRICAL FORCE FIELD FROM DENSITY FUNCTIONAL ENERGY SURFACES**

Empirical force fields are used extensively to model organic systems, and their theoretical foundation, range of applicability and computational implementations are well documented [10]. All represent intra-molecular bonding by mechanical analogs (bonds, restoring forces, excluded volume), and inter-molecular interactions by Coulomb, dispersion, and short-range interactions. The evaluation of the potential energy and interatomic forces is orders of magnitude faster than by DF, and this extends significantly the range of sizes and times amenable to simulation. The efficiency is achieved at the expense of fully quantitative accuracy and predictive power, which remain particular strengths of DF. The balance between efficiency and quantitative accuracy is moved even farther towards simplicity by generic potentials, which aim to describe large classes of materials (e.g., all organic systems) by a functional form with a fixed (although often very large) set of parameters defining specific interatomic interactions.

Quantitative accuracy can be obtained by tuning these models for specific systems or for well defined chemical and thermodynamic conditions. However, the large number of free parameters and the lack of accurate information on the potential energy surface often make this difficult. The availability of an extended data base of DF results overcomes the second problem and can ease the first, since a detailed knowledge of the potential energy surface makes it possible to identify situations that define specific parameters. Their determination can then be decoupled from a global fit to the potential energy surface. For instance, an accurate determination of ground state structures defines most of the geometrical parameters necessary, while the availability of all harmonic eigenfrequencies and eigenvectors allow the corresponding force constants to be determined.

We have based this aspect of our work on a generic model (Tripos) [11] that had been used previously for BPA-PC. The low polarity of these molecules is confirmed by low values of the dielectric constant), and we have not included electrostatic charges. We have assumed that intermolecular interactions are due solely to dispersion forces and short range repulsions [12]. Comparison of the Tripos predictions with DF results shows that ground state geometries are described fairly well by this force field, while the vibrational frequencies are overestimated significantly. The latter problem can be solved by rescaling the model force constants (see Fig. 3). Particularly important is the fine tuning of the intermolecular interactions that determine the barrier for the phenylene π-flip in DPBC crystals: The overestimate of this barrier by almost a factor of three can easily be corrected by redefining the short range H-H and H-O repulsions.

The improved potential has been used in extensive MC simulations of 72 DPBC molecules
(4248 atoms), and for MD simulations of BPA-PC chains for systems of $\sim 30000$ atoms. The speedup with respect to DF can be appreciated by noting that these last computations were performed with relatively inexpensive single CPU workstations, while the DF study of molecular crystals with 236 atoms required long runs on a massively parallel computer. The gain in simulation time is even more dramatic, increasing from a few picoseconds in DF calculations to well beyond the ns range with parameterized force fields. These gains are particularly important for amorphous and inhomogeneous systems, which are characterized by large distances and long relaxation times. To illustrate this point we now discuss the determination of the glass transition temperature of DPBC.

The quench of liquid DPBC results in an amorphous system below a glass temperature $T_g$ that manifests itself with a rapid increase of viscosity, and with the (nearly) discontinuous change of the specific heat $C_p$ and thermal expansion coefficient $\chi_T$. A liquid sample of 72 DPBC molecules well equilibrated at 700K is quenched progressively by MC in a sequence of runs ($3 \times 10^6$ MC steps), during each of which $T$ is lowered discontinuously by 10 K. The entire quench takes $200 \times 10^6$ MC steps, and results in a low temperature structure that is apparently disordered.

Although the potential energy $U$ is a remarkably linear function of $T$ both at low and high temperatures, a linear fit of the low (150 – 300 K) and high (550 – 700 K) temperature behavior of $U(T)$ allows us to identify a change in the constant pressure specific heat at $T \sim 400$ K (Fig. 4). The crossing of the two lines at $T = 410$ locates the glass point of the model. A similar behavior is displayed by the temperature dependence of the volume at zero pressure (Fig. 4) : at high $T$ we find a larger thermal expansion coefficient than at low $T$. The crossing of the linear parts of $V(T)$ at $T = 440$ K provides a second estimate of $T_g$. The values based on specific heat and thermal expansion coefficient bracket the experimental values of the glass temperature for BPA-PC (418 – 432 K).

Figure 3: Calculated vibration spectra of DPBC. Left to right: DF calculations, refined fit, and Tripos.
REACTIONS OF PHENOXIDES WITH CYCLIC TETRAMER

The importance of chemical reactions for the production, chemical stability and recycling properties of polymers contrasts starkly with the few computational studies of these processes. Most parameterized force fields assume as fixed bonding pattern and are unable to deal with chemical reactions. DF schemes, on the other hand, are well suited for this purpose, because they describe explicitly the electronic degrees of freedom responsible for chemical transformations. However, while DF calculations are widely recognized for predicting equilibrium properties for systems close to their optimal bonding state, their accuracy for bond formation and breaking is much less established. To enhance our understanding of the reactivity of polycarbonates and to gain experience in the ability of DF to describe this, we have studied a series of reaction steps involving simple polycarbonates and other chemical species used in industrial processes [13].

An interesting example of an application is the ring-opening polymerization of BPA-PC from cyclic oligomers, using nucleophilic molecules as catalysts. Examples of these are lithium and sodium phenoxide (LiOPh and NaOPh, respectively). Our detailed studies of the cyclic BPA-PC tetramer have shown that this molecule is strain free and representative of larger species, and we have used it as a model in this context, and its reaction with LiOPh and NaOPh follows the path illustrated in Fig. 5. Chemical considerations suggest that an attack involving the (positively charged) metal atom will take place at the carbonate group, and we have investigated the reaction by performing a constrained simulation using the distance $R_C$ between the carbonyl carbon and the reactant O as reaction coordinate.

Fig. 6 shows six snapshots of the trajectory for the reaction of LiOPh initially outside the cyclic tetramer. The two molecules interact weakly for $R_C \sim 4$, with steric interactions giving rise to an

Figure 4: Variation of potential energy $U$ and volume $V$ with temperature $T$. 

[Graphs showing variation of potential energy and volume with temperature]
energy barrier of 4 kcal/mol at $R_C = 3.8 \, \text{Å}$. For shorter separations, the Li-O attraction induces a rotation of the carbonyl group and a rapid decrease ($\sim 15$ kcal/mol) in the potential energy. The energy stays below the initial value as $R_C$ is reduced to $\sim 1.8 \, \text{Å}$, where the C of the original carbonate is surrounded by four O atoms with approximately tetrahedral coordination ($C_T$). The formation of this configuration (Fig. (c)) is accompanied by an increase in all $C_T - O$ distances, since the electrophilic Li atom is shared between the original O of LiOPh and the O atom formerly in the carbonyl group. $C_T$ has a large positive charge, while the four O atoms are nearly equivalent, with charges similar to those of other tetrahedral O atoms in the chain. A reduction of $R_C$ to $1.5 \, \text{Å}$ (corresponding to a second energy barrier of 4 kcal/mol) is required to symmetrize the tetrahedral geometry of $C_T$ and to break the symmetric bonding of Li. The Li is now attached to the tetrahedral O that is bound to a single C atom (Fig. 6(4)). The Li-O bond is oriented along one of the three $C_T$-O bonds, because of the electrostatic attraction between the positive Li and the electron charge in the covalent bonds. Nevertheless, the $C_T$-O bond provides a 3-fold axis for rotations of the O-Li bond, that give rise to potential energy variations of 1 kcal/mol at most.

Under normal thermodynamic conditions, the O-Li bond can then be oriented with equal probability along the three directions specified by the $C_T$-O bonds at the base of the tetrahedron. Relaxation of the two equivalent structures with the O-Li bond oriented along a $C_T$-O bond different from the original one gives rise to structure 6(6), which has a weak bond between Li and the new carbonyl O. At room temperature, this weak bond should break easily, leading to the open chain with an active -C-O-Li termination. In agreement with experimental evidence, this last configuration has virtually the same potential energy of the reactants. Moreover, the chain termination reproduces the structure and chemical characteristics of the original LiOPh, and, therefore, it could catalyze the ring opening of further oligomers, giving rise to a “living polymer”.

Similar results have been obtained for different initial configurations of the reactants, for the reaction involving NaOPh, and for a variety of different BPA-PC fragments and different reactants. A notable exception is the reaction of the cyclic tetramer with phenol. Although similar to LiOPh and NaOPh, phenol does not react with BPA-PC chains unless the energy increases to values incompatible with a reaction at accessible temperatures.
POLYMERIZATION OF POLYCARBONATE: MODEL SIMULATIONS

The analysis of the reaction between the cyclic tetramer and reactants like LiOPh and NaOPh clarifies the origin of their catalytic activity, and provides much information about the reaction mechanisms. However, it does not explain the reason why cyclic oligomers do polymerize under the appropriate chemical conditions, since reactants and products have nearly the same potential energy. The vibrational properties that determine configurational entropy contributions also change little during the reaction.

To investigate the nature of the driving force leading to polymerization, we have used a simplified model, in which BPA-PC structural units are represented by Lennard-Jones particles connected by harmonic springs representing covalent bonds in the polymer backbone. Each particle forms either one or two bonds so that the system comprises open chains and rings without branching. The catalyst is represented by active particles, which can interchange their bonds with a neighboring particle. The active particles can form only one bond, so that they are always located at an end of a chain with at least two particles. The rules for the bond interchange are shown in Fig. 7, which illustrates the two basic processes that take place with equal probability, i.e., the incorporation (Fig. 7(a)) and the separation (Fig. 7(b)) of a ring from an open chain carrying an active head. These processes conserve the number of bonds and reproduce the basic feature of the BPA-PC reaction described above. Simulations are performed by a Monte Carlo method sampling both the positions and bonding configuration using a Metropolis algorithm.

AA3.1.8
We have investigated systems in 2D and 3D over a wide range of densities and temperatures, focusing on the limit of low catalyst concentration by introducing a single active particle in systems with 10001 normal ones. All computations were started by equilibrating a sample of 2500 cyclic tetramers before introducing a single dimer carrying one active particle. According to the above rules, the system can develop into an assembly of rings of variable length and one open chain terminated by the reactive head. We discuss in detail the results in 2D, because they are the easiest to report in graphical form, and because they are presumably the least affected by finite size effects, that are instead the major source of error for the 3D simulations. In most cases, the catalyst has a dramatic influence on the configuration, as can be seen in Fig. 8, which shows snapshots of the original assembly of tetramers and of the same system after a long equilibration.

Figure 7: Model used to study polymerization: (a) chain formation from ring, (b) ring formation from chain. The active site is denoted by an open circle.

Figure 8: Snapshots of (a) the initial tetramer fluid and (b) a configuration at equilibrium under the bond interchange mechanism for a 2D system $\eta = 0.4$ and $T = 3$. 
The most important parameter governing polymerization is the density. In Fig. 9 we show the average length of the active chain as a function of density and temperature, and we see that the effect of temperature is relatively weak. The discontinuity in the density dependence, on the other hand, suggests that polymerization occurs via a first order transition. The probability distribution for the size of either cyclic and open chains is broad, since incorporation and separation processes occur frequently, and each of them can change significantly the size of the reacting polymers. These reasons underly the easy reversibility of polymerization. We have tested this by changing the density across the polymerization line and observing the growth of the active chain when density is increased, or its collapse when it decreases below the polymerization threshold.

![Diagram](image)

Figure 9: Comparison of the average length of the active chain in 2D as a function of (left) packing fraction at $T = 3$, (right) $T$ for $\eta = 0.4$.

The simulations in 3D and 2D show similarities as well as differences. Simulations in 3D show that the tendency towards the polymeric state is much stronger in 3D than in 2D, with the average mass of the active chain being well beyond 50% of the total in most of the simulations. This massive polymerization, however, implies that the results are affected by large finite size effects, since the polymeric chains would grow even further in larger systems.

The average polymer length increases with increasing density and, to a lesser degree, with increasing $T$. The saturation in the degree of polymerization evident at the upper limit of the density and temperature ranges could be due to finite size effects. The average size of rings is again roughly two orders of magnitude smaller than the average length of the open chain, but in 3D the total mass of the rings is somewhat less than in the active chain. Both in 2D and 3D we observe a systematic and very significant increase of viscosity and a decrease in diffusion during polymerization.

These results allow us to discuss the driving force behind the transition. We have noted that the model does not introduce a significant thermodynamical bias with respect to the polymer size, with the possible exception that very small rings are less favored. Since the potential energy rises on polymerization, the transition must be due to an entropy contribution related to the bond interchange mechanism. First, the mechanism allows a wide range of polymer sizes to be explored, thus increasing enormously the number of possible configurations. Moreover, in dense homoge-
neous systems the number of long, open chains of bonds connecting nearest neighboring particles is exponentially larger than the number of short cyclic paths. The formation of long chains, however, reduces the long range mobility of particles (as shown by the strong decrease in the diffusion coefficient) that is another crucial source of entropy. As a result, polymerization prevails at high density, when long range mobility is already prevented by packing. The importance of the mobility of short chains at low density is reflected in the decline of polymerization. The rapid increase in the number of long open paths with the number of neighbors within a bonding distance also explains the greater tendency to polymerization found in three dimensions.

Additional contributions will be provided by dynamical effects, since the local mobility of particles is less constrained in long open chains than in short cyclic ones. Again, the optimization of local mobility (leading to polymerization) prevails at high density, when the long range mobility is ineffective. These considerations all suggest a similarity with crystallization[14], which occurs even for hard spheres when the potential energy is identically zero and so must be entropy driven. Crystallization can be understood as a similar competition between short and long-range constraints, and this parallel supports our identification of polymerization as a first-order transition. It also indicates why density is much more important than temperature.

CONCLUSIONS

A hierarchy of approximations has been used to investigate structural and thermodynamic properties of polycarbonates, covering a range of size scales from atomistic to mesoscopic. The microscopic level is the domain of DF computations, which provide a reliable description of geometries, potential energy surfaces, and low energy dynamical properties. This information is the basis for building and testing empirical interatomic potential models that extend the reach of simulation up to the mesoscopic range. This opens the way for the investigation of mechanical and thermal properties, as well as for the simulation of inhomogeneous systems such as surfaces and interfaces.

The investigation of chemical transformations requires again the application of DF methods, in order to determine the basic reaction steps relevant for the material of interest. Realistic material science problems, however, require this information to be incorporated into simplified models that can account for thermal and statistical effects. We have illustrated this using the polymerization of carbonate oligomers: DF calculations identify the basic reaction step, which is then reproduced by an idealized model. Simulations with this model provide a direct view of polymerization and allow us to identify the driving force behind this transformation, and to investigate the role of temperature, density and dimensionality in this process.

The expected increase of computer power and the rapidly growing experience in this field will extend the range of problems amenable to such approaches. They should provide a valuable complement to other methods used to investigate the mechanical and thermal properties of polymers under a wide variety of conditions, both equilibrium and non-equilibrium.

References

[*] Permanent address: Università degli Studi di Messina, Dipartimento di Fisica, I-98166 Messina, Italy.
[9] Computations have been done with the CPMD program version 3.0, Hutter, J. et al., Max-Planck-Institut für Festkörperforschung and IBM Research 1990-99.