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# Density functional/Monte Carlo study of ring-opening polymerization

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## Abstract

Density functional calculations of the structure, potential energy surface and reactivity for organic systems closely related to bisphenol-A-polycarbonate (BPA-PC) provide the basis for a model describing the ring-opening polymerization of its cyclic oligomers by nucleophilic molecules. Monte Carlo simulations using this model show a strong tendency to polymerize that is increased by increasing density and temperature, and is greater in 3D than in 2D. Entropy in the distribution of inter-particle bonds is the driving force for chain formation. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The wide range of applications of polycarbonates is a consequence of their outstanding mechanical, optical and thermal properties. Although polycarbonates have been produced and processed on an industrial scale for decades, important questions remain concerning the relation between their macroscopic properties and the atomistic structure. An example is the polymerization of cyclic oligomers of bisphenol A polycarbonate (BPA-PC) to long chains and rings, whose size distribution is crucial to determine the thermal and mechanical properties. A detailed understanding of this process requires a multifaceted investigation covering elec-

tronic and structural properties, chemical kinetics, and statistical mechanics. We describe here such a computational investigation of one route to BPA-PC, the ring-opening polymerization of its cyclic oligomers using small metallo-organic, nucleophilic molecules as catalysts [1].

The basic reaction step has been investigated by combined density functional (DF)/molecular dynamics computations [2], which provide reliable predictions of reaction pathways and energies for these systems. The effect of many such reactions occurring in a condensed environment has then been investigated by Monte Carlo computations for a model based on the DF results, which also provide key parameters for our simulations. Our assumption of equilibrium polymerization is not strictly valid for the conditions applicable in industry, but it allows us to use standard statistical mechanics approaches.

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The present simulations describe a “living polymer” that both differs from and is similar to other models investigated in recent years [3,4]. The combination of the DF computations and classical simulations allows us to identify the driving force for polymerization and to investigate the effect of thermodynamical conditions, dimensionality (2D and 3D), and of the relative concentration of reactants and catalyst.

## 2. Reactions of phenoxides with cyclic tetramer

The ring-opening polymerization of cyclic oligomers of BPA-PC is catalyzed by nucleophilic molecules such as lithium and sodium phenoxide (LiOPh and NaOPh, respectively). Our DF calculations of the cyclic BPA-PC tetramer have shown that the local coordination of this molecule is very similar to that in the PC chains, and its reaction with LiOPh and NaOPh follows the path illustrated in Fig. 1 [5]. An attack involving the (positively charged) metal atom is most likely at the carbonate group, and we have investigated the reaction by performing a constrained simulation using the distance  $R_C$  between the carbonyl C and the reactant O as reaction coordinate.

Fig. 2 shows six snapshots of the trajectory for the reaction of LiOPh approaching from outside the cyclic tetramer. Details are given in Ref. [5] and are summarized here. The reactants interact weakly for  $R_C \sim 4$ , with steric hindrances giving rise to an energy barrier of 4 kcal/mol at  $R_C = 3.8$  Å. For shorter separations, the Li–O attraction induces a rotation of the carbonyl group and a rapid decrease

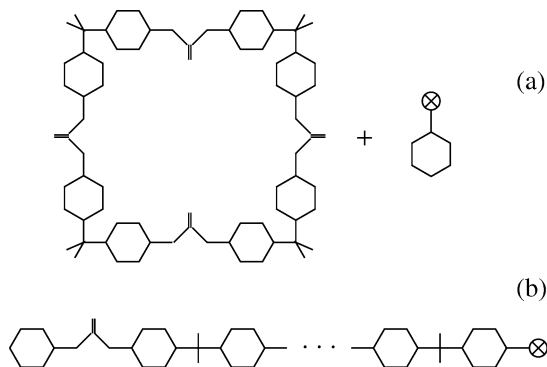


Fig. 1. Scheme of ring-opening reaction of cyclic tetramer with LiOPh (Li atom crossed).

( $\sim 15$  kcal/mol) in the potential energy [2(2)]. Smaller values of  $R_C$  lead to a C atom surrounded by four O atoms with approximately tetrahedral coordination [2(3)]. A reduction of  $R_C$  to 1.5 Å (corresponding to a second energy barrier of 4 kcal/mol) breaks the symmetric bonding of Li, and the Li is now attached to the tetrahedral O bound to a single C atom [2(4)]. This bond provides a 3-fold axis for rotations of the O–Li bond that result in very small energy variations.

Under normal thermodynamic conditions, the O–Li bond can then be oriented with equal probability along three directions. One relaxation gives rise to structure 2(6), which has a weak bond between Li and the new carbonyl O. This weak bond will break at room temperature, leading to the open chain with an active –C–O–Li termination. This last configuration has essentially the same potentially energy as the original reac-

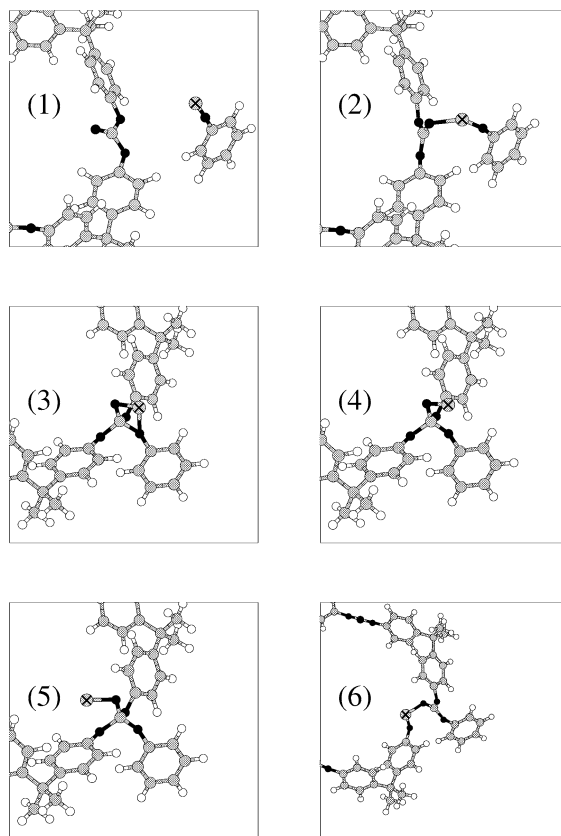


Fig. 2. Reaction of LiOPh with cyclic tetramer of BPA-PC. The product (6) is a Li-terminated chain (Li atom crossed). Only part of the chain is shown.

tants, in agreement with experimental evidence. Moreover, the chain termination reproduces the structure and chemical characteristics of the original LiOPh. It could catalyze the ring opening of further oligomers, giving rise to a “living polymer”.

### 3. Polymerization of PC: Model simulations

The analysis of the reaction between the cyclic tetramer and LiOPh and NaOPh clarifies the origin of their catalytic activity, and provides much information about the reaction mechanisms. However, it does not explain why cyclic oligomers polymerize under appropriate 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 the covalent bonds in the polymer backbone. Each particle forms one or two bonds so that the system comprises open chains and rings without branching, and the catalyst is represented by *active* particles that can interchange their bonds with a neighboring particle. The active particles can form only one bond, so that they must be at an end of a chain with at least two particles. We described recently calculations where we assumed the presence of a single active particle [6], and we now extend these calculations to multiple active sites.

The rules for bond interchange are shown in Fig. 3, which illustrates the three basic processes taking place: the incorporation [3(a)] and the separation [3(b)] of a ring from an open chain carrying an active head, and the interchange of segments between chains [3(c)]. These processes conserve the number of bonds and reproduce the basic feature of the BPA-PC reaction described above. Monte Carlo simulations are performed by sampling the positions and bonding configuration using a Metropolis algorithm.

We have investigated systems in 2D and 3D over a wide range of densities and temperatures, focusing on the limit of low catalyst concentration (from 0.01 to 0.36%). All computations were started by equilibrating a sample of 2500 cyclic tetramers before introduc-

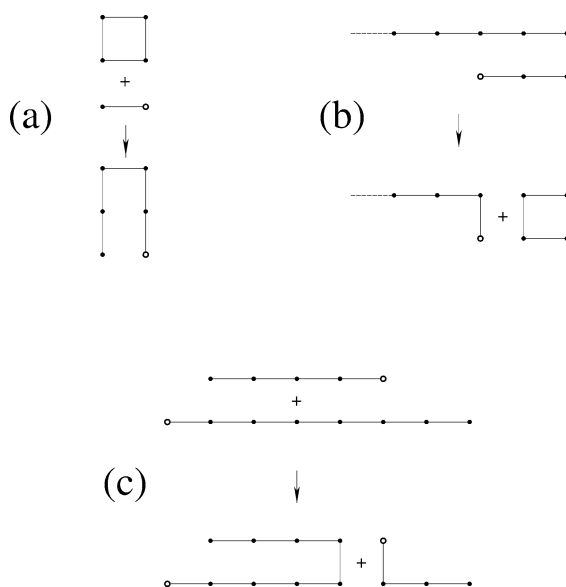


Fig. 3. Model used to study polymerization: (a) chain formation from ring, (b) ring formation from chain, and (c) tail interchange between active chains. The active site is denoted by an open circle.

ing a small number (from 1 to 36) of dimers, each with one active particle representing the metal termination of the M-OPh molecule. The primary role of the catalyst is to enhance the kinetics of the rearrangement of the covalent bonds. However, since the number of bonds is conserved during ring-opening polymerization of BPA-PC, the number of catalyst molecules also determines the number of free chain terminations (active or not) in the system, which is conserved during the entire polymerization process. Only the second effect plays a role in our MC simulations, since at equilibrium the results cannot depend on kinetics.

In most cases, the addition of the catalyst to the system of tetramers influences the configuration dramatically, giving rise to long open chains including ~50% of the particles in the system (see Fig. 4). The remaining particles are subdivided into an equilibrium population of rings, whose average size is much smaller than that of the chains.

The results in two dimensions, which are less affected by finite-size effects than their three dimensional counterparts with the same particle number, are discussed first. We also emphasize open chains more than rings, because only the former reach the lengths relevant for applications. To compare results in 2D and

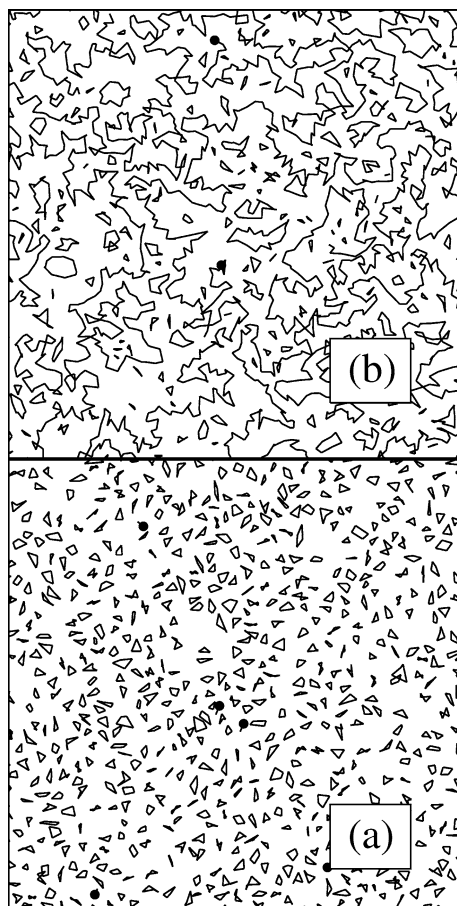


Fig. 4. Snapshots of (a) the initial tetramer fluid, and (b) a configuration at equilibrium under the bond interchange mechanism. Simulation in 2D at  $\eta = 0.4$  and  $T = 3$ . Solid dots identify active particles.

in 3D, we express densities in terms of the packing fraction  $\eta$ , defined as  $\eta = \pi\rho\sigma^2/4$  and  $\eta = \pi\rho\sigma^3/6$  in 2D and in 3D, respectively, where  $\sigma$  is the Lennard–Jones diameter of our particles.

In Fig. 5 we show the average length of the active chain  $N_a$  as a function of density for different concentrations of active particles. The degree of polymerization increases with increasing density, with a sharp rise at  $\eta \sim 0.15$ . The competition between active chains for the available monomers means that the average chain length decreases with increasing concentration of the active particles. The average chain length scales almost exactly as  $1/N_a$  at high density, implying that the total mass in the polymer phase is independent of  $N_a$ . The increasing average length with decreasing  $N_a$

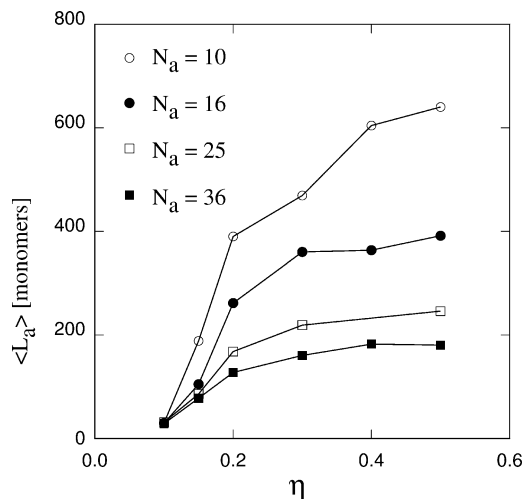


Fig. 5. Average length of active chains as a function of packing fraction  $\eta$  for different concentrations  $N_a$  of active particles.

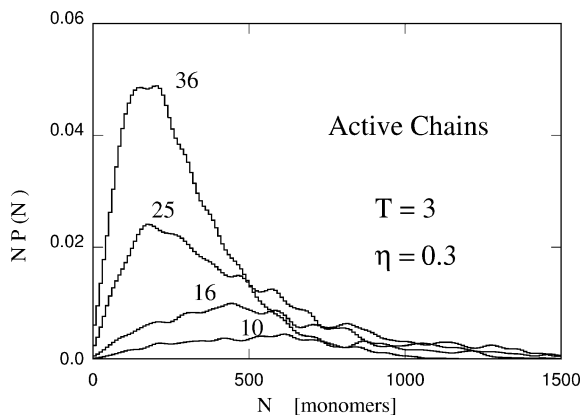


Fig. 6. Size distribution of active chains with different numbers  $N_a$ .

makes the rise at  $\eta = 0.15$  more pronounced, leading to a discontinuous transition in the limit of vanishing concentration of the catalyst [6]. The probability distribution for the size of either cyclic and open chains is broad, since incorporation and separation processes occur frequently, and both can change significantly the size of the reacting polymers. This can be seen in Fig. 6, which shows the size distribution  $P(N)$  of the chains for different values of  $N_a$ . The size distribution of the rings is much narrower, and depends very little on either density or  $N_a$  (see Fig. 7).

Fig. 8 shows that  $T$  also affects the average length of the chains, although less dramatically than the density. The monotonic rise of the polymerization

degree with increasing  $T$  is a first indication that entropy is the driving force stabilizing the long chains.

The simulations in 3D and 2D show similarities as well as differences. The tendency to polymerize is much stronger in 3D, with the average mass of the active chain generally being well above 80% of the total, and the polymerization line occurs in 3D at a packing fraction an order of magnitude lower. In both 2D and 3D we observe a systematic and very significant increase of viscosity and a decrease in diffusion during polymerization.

The results show that the driving force behind the transition must be an entropy contribution related to the bond interchange mechanism, since the model does not introduce a significant thermodynamical bias

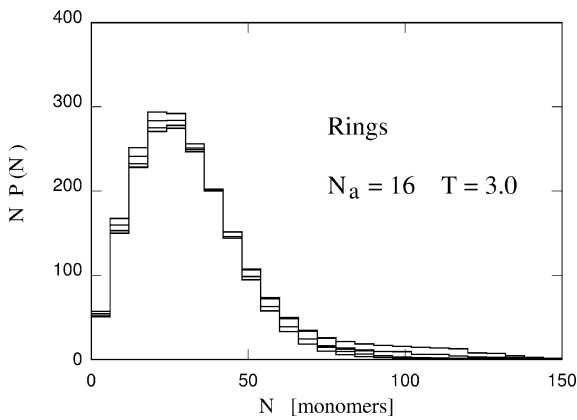


Fig. 7. Size distribution for rings in 2D simulations at different packing fractions  $0.1 \leq \eta \leq 0.5$ .

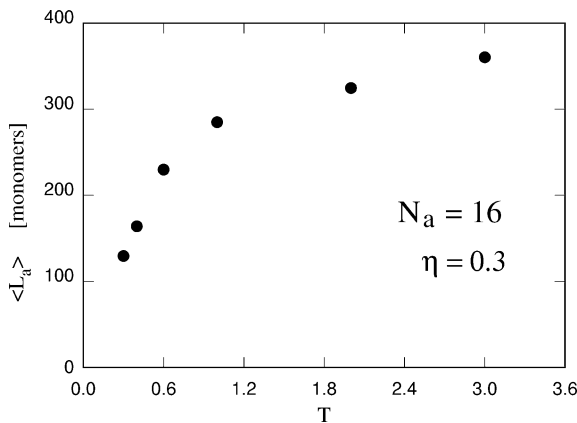


Fig. 8. Average length of active chains as a function of temperature (2D).

with respect to the polymer size, and the potential energy rises on polymerization. First, the mechanism allows a wide range of polymer sizes to be explored and increases enormously the number of possible configurations. Moreover, in dense homogeneous systems the number of long, open chains of bonds connecting nearest neighbors is exponentially larger than the number of short cyclic paths. However, the formation of long chains reduces the long range mobility of particles (as shown by the strong decrease in the diffusion coefficient), which is an important 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 increasing number of neighbors also explains the greater tendency to polymerization found in three dimensions.

These considerations suggest a similarity to crystallization [7], which is entropy driven because it occurs even for hard spheres when the potential energy is identically zero. Crystallization can also be understood as a competition between short and long-range constraints, and this parallel supports our identification of polymerization as a phase transition and indicates why density is a more important variable than temperature.

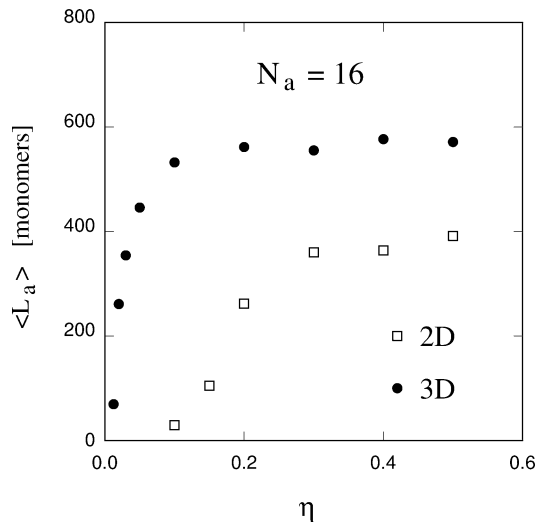


Fig. 9. Comparison of the average length of the active chains as a function of packing in 2D and in 3D.

#### 4. Discussion and concluding remarks

A combination of DF computations and MC simulations has been used to investigate ring-opening polymerization in BPA-PC. Density functional calculations have been used to determine the energy balance, the reaction barrier and the path for the basic step leading to polymerization. A model incorporating these ingredients and energy parameters identified by the DF computations has been devised. Extensive MC simulations show that, although energy and vibrational entropy are unchanged by the chemical reaction, the model displays a strong tendency to form long chains that is enhanced further by increasing density, temperature and dimensionality. Polymerization in 2D gives rise to a discontinuous transition as a function of density in the limit of vanishing concentration of catalyst molecules. In 3D a similar transition occurs at much lower density than in 2D. Increasing  $T$  increases the degree of polymerization in both 2D and 3D.

These features, together with the analysis of thermodynamic functions and dynamical properties (diffusion and viscosity), show that the entropy in the distribution of inter-particle bonds is the driving force for chain formation, and they suggest an analogy between

polymerization and crystallization. We are investigating the effect of a small concentration of trifunctional units on the size and connectivity of the polymers.

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