

# Reactive force field for electrophilic substitution at an aromatic system in twin polymerization



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## ABSTRACT

Twin polymerization is a new synthesis concept, which enables the formation of two different macromolecular structures from organic–inorganic hybrid materials in one single process step. To gain insights into formation processes we implement a first-principles-based ReaxFF reactive force field for C/H/O/Si for the initial electrophilic substitution of an aromatic system. We show that established parametrizations that have been developed to model chemical reactions of (hydro) carbon or carbon nanotubes systems successfully cannot reproduce this reaction although they include the same chemical elements and in parts same reaction mechanisms. Thus, we develop a new parametrization being capable in reproducing this aromatic reaction properly and compare it to the established ones to identify the differences.

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## 1. Introduction

Polymer hybrid materials, i.e. materials combining organic polymer structures with inorganic components on the nanoscale, play an important role in reinforcing, coating and barrier materials. The production of such nanostructured polymer hybrid materials is a challenging task, since two different components must be merged together, while suppressing phase separation processes on the molecular level. The established way is either a simultaneous polymerization of two different monomers in one procedure or the chain (or step-growth) polymerization of heterobifunctional monomers, where each polymerizable functional group [1,2] of these monomers polymerizes independently and by another mechanism.

In recent years [3–5] a more elegant technique called twin polymerization has been developed to synthesize these hybrid materials with organic and inorganic structure domains. Twin polymerization is a special process, that utilizes twin monomers containing differently polymerizable groups in one molecule, where only one initialization step is necessary to start the process.

A typical twin monomer structure features a metal center, like Si, representing the inorganic part and two organic structure components as shown in Fig. 1(a). In that figure the structure of the twin monomer 2,2'-spirobi[4H-1,3,2-benzodioxasiline] (1) is shown that has been extensively investigated in experiments [6,3–5,7,8].

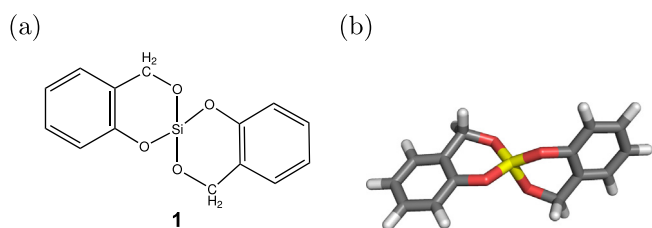
Such twin monomers undergo polymerization into two different polymers in one process, where the polymerization processes are mechanistically coupled. The decoupling of the monomers to several molecular fragments during the polymerization process, i.e. the organic and inorganic network, yields the difference to the repeating unit in established chain (or step-growth) polymerization processes [9].

Due to the intrinsic coupling of different structure elements a special feature of the polymers obtained by twin polymerization is that the inorganic and the organic structure domains have a defined size of 0.5–3 nm [6]. Thus, polymer hybrid materials structured on the nanoscale can be created. Then, just a simple post-treatment, like combustion of the organic phase or HF treatment of the inorganic phase [4] is necessary in order to obtain nanoporous carbon or oxide structures that may lead to new polymer- and metal/transition metal oxides [10,11].

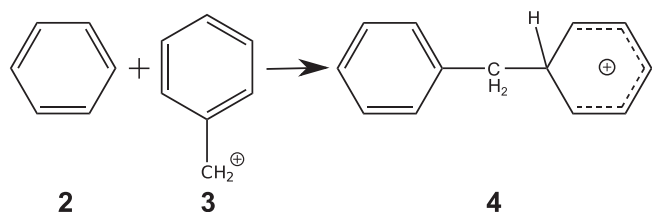
The theoretical understanding of the overall twin polymerization process and especially of the structure formation of the composite material is still at the beginning. Twin polymerization is

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**Fig. 1.** The scheme of the typical twin monomer 2,2'-spirobi[4H-1,3,2-benzodioxasiline] (**1**) is depicted in (a) and its steric structure in (b). Note that yellow represents Si elements, red O, gray C and white H. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 2.** The reaction scheme of our test system consisting of benzene and benzyl cation for further investigations is presented.

based on concurring processes, including many different reaction steps. Due to quantum chemical calculations [6] it is assumed, that at first the formation of the organic structure, a phenolic resin, starts and then time-delayed the formation of the metal oxide follows.

It is our aim to assist understanding the structure formation of the composite materials. Therefore, simulation of twin polymerization at an atomic level using reactive molecular dynamics simulation with ReaxFF is utilized, as it can provide new insights into this complex polymerization process. In this paper we focus on one single reaction step: The initial formation of a carbon–carbon bond between two twin monomers. This partial reaction is essential for the subsequent formation of the organic network. To investigate this reaction in detail we introduce a smaller test system with benzene (**2**) and benzyl cation (**3**), shown in Fig. 2. These two structures represent the essential reacting components of the twin monomers to form the carbon network and they contain the pure organic components of the twin monomer. After investigating and reproducing the bond formation between benzene and benzyl cation, we adopt the findings for our analysis of the C–C formation of two twin monomer structures, in order to find an appropriate ReaxFF parameter set for the reaction of the twin monomer as well as for the benzene system. Thereby, it becomes apparent that we can model the bond formation in both systems appropriately by the same parameter set.

The paper is organized as follows: First we give a short theoretical introduction to twin polymerization, the twin monomer and the benzene system. Then, the computational method ReaxFF is described. We continue to analyze and discuss the simulation results of the aromatic C–C bonding for the benzene system as well as for the twin monomer. A summary is given at the end.

## 2. Twin polymerization

The steric structure of **1** is given in Fig. 1(b), where the Si atom is the central metal fragment that connects to two benzene rings by two different bridging units, O–CH<sub>2</sub> bonds and direct O bonds. A special aspect of these structures is that the bridges feature

different stability concerning the proton catalyzed initiation steps, as reported in Spange et al. [6].

A first discussion about the reaction mechanism of the twin polymerization was given in Spange et al. [6]. There, first reaction steps of the twin polymerization are discussed and structures to be obtained after certain partial reactions are presented. As we utilize this reaction mechanism as a basis for our modeling, we give a brief review of the occurring reaction steps.

In [6] it is assumed that the twin polymerization starts with an acid catalyzed cleavage of the O–CH<sub>2</sub> bond to form an electrophilic benzyl cation (**5**) (Fig. 3(a)). This reaction is favored due to the resonance stabilization of the benzyl cation. After the formation of a van der Waals complex ( $\pi$ -complex), the electrophilic CH<sub>2</sub><sup>+</sup> group reacts in an electrophilic substitution with the benzene ring of a second twin monomer leading to the more stable  $\sigma$ -complex (**6**), given in Fig. 3(b). The subsequent rearomatization restores the  $\pi$ -complex (**7**) by dissociation of the proton from the aromatic ring. This provides a H<sup>+</sup> and in this way the catalyst is recovered (Fig. 3(c)).

After the formation of the organic network has started, the cleavage of the Si–O bonds and thus the oxide formation begins. This process step provides the phenolic OH group. In Spange et al. [6] it is expected that the propagation of the electrophilic substitution is significantly faster than this step. This enables the substitutions prior to complete separation of the molecule, i.e. the separation of the organic network. As a result the interweaved organic–inorganic nanoporous structure is formed. In the following, we concentrate on the initialization of the organic network formation due to formation of **6**.

One can see that due to the complex structure of **1** there are concurring effects of the organic and inorganic components that influence the reaction mechanism. In the case of the carbon–carbon formation we focus on, we have influences of the oxygen in the bridging units and the Si-central metal component both being close to the reaction center. However, as the reaction itself only take part between the organic components of **1** we reduce the complexity of the problem. We first simplify **1** to its pure CH components, which are assumed to be the reaction centers. This is done by using a benzene ring (**2**) with a benzyl cation (**3**) (Fig. 2), in the following called benzene system. As the system contains only C and H, we are able to review the impact of the aromatic rings on the electrophilic substitution independently of the O and the Si components.

The obtained results were then used as starting point for our investigation of **1** to understand and reproduce the C–C bond formation of **1** (Fig. 3(b)). In this process it becomes apparent that the C–C formation between **1** and **5** as well as between **2** and **3** can be modeled appropriately with the same parameter set, introduced below.

## 3. Computational details

### 3.1. ReaxFF

As mentioned in the beginning it is our long term goal to understand the twin polymerization process at an atomic level, to gain insights into reaction mechanism and the formation of the resulting nanoporous structure. Therefore, oligomer to polymer systems are needed in the simulation model.

Quantum chemistry approaches can provide energy surfaces and geometries of small molecular systems sufficiently accurate to give hints on a reaction mechanism in advance of experiments. The scaling of the computational cost with system size limits these methods to small systems and therefore they are unsuitable for modeling polymer systems. With coarse grained models [12,13]

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