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Peri-condensed aromatics with aliphatic chains as key intermediates for the nucleation of aromatic hydrocarbons

Seung-Hyun Chung, Angela Violi *

Department of Mechanical Engineering, University of Michigan, Ann Arbor, MI 48109-2125, USA

Abstract

Soot nucleation bridges the transition from gaseous hydrocarbons to macromolecular building blocks (nanoparticles) that eventually turn into soot. Polycyclic aromatic hydrocarbons (PAH) have often been invoked as important compounds of this process but their role has not been clearly identified. In this paper we report on a detailed analysis of the physical interactions between PAH in the range 200–450 amu using Molecular Dynamics simulations. In particular, we identified a pool of nine aromatics and studied their clustering behaviors in systems composed of thousands of homo-molecular and hetero-molecular molecules to understand the influence of molecular mass, morphology and temperature on the nucleation process. At temperatures higher than 1000 K, small clusters of PAH (2–5 molecules) are detected but they are not stable enough to accommodate the further growth into larger particles. This result raises doubts on the ability of these molecules to become soot nuclei. Molecular morphology is another important parameter for the nucleation process. Aromatics with attached aliphatic chains show considerably faster nucleation rates than the corresponding polycyclic aromatic hydrocarbons of similar mass without any chain. The collision efficiency is not increased by the aliphatic chain attachments, which may indicate that a faster nucleation process for these systems is due to the ability of these molecules to accommodate the collision energy into additional internal vibrational modes of the aliphatic chains. The results of this study provide information on the clustering behavior of PAH and can lead to the development of a more complex model to describe the physical nucleation of PAH that includes molecular masses, morphologies and temperature as main parameters to describe the transition from gas-phase species to macromolecular structures.
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1. Introduction

Mechanisms of soot formation have been studied for quite some time, and there is general consensus that polycyclic aromatic hydrocarbons (PAH) are key intermediates: their growth leads to nucleation of particles and the latter continue to add mass via surface growth [1–6].

The transformation from PAH to soot has been often described as a purely chemical growth by many researchers [7–16]. Aromatic precursors grow in size due to chemical reactions and by virtue of the increasing size, the species acquire the property of a condensed phase. During the

* Corresponding author.
E-mail address: avioli@umich.edu (A. Violi).

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molecular growth process, however, the magnitude of non-bonded interactions between structures can become large enough so that chemical bonding is no longer a requirement for sticking. In particular, the attractive interactions between pi electrons in aromatic systems are among the strongest non-covalent interactions in nature. Therefore, in addition to chemical growth mechanisms of PAH, various studies have been reported on physical coagulation of aromatics [17–33]. Schuetz and Frenklach [17] studied the lifetime of pyrene dimers in flame conditions using Molecular Dynamics simulations with semi-empirical force fields and concluded that the internal rotations of the colliding pair extended the lifetime of dimers. Thus the onset of PAH condensation may occur for small compounds. A similar study was reported by Wong et al. on aromatic molecules linked by aliphatic chains and peri-condensed aromatics [18], showing that the first class of molecules produces dimers faster than the equivalent condensed aromatics. Miller and co-workers [19,20] have reported detailed calculations of the intermolecular potentials for clusters of PAH from 78 to 1830 Da, showing that the binding energies rise with molecular size and asymptotically approach the experimentally value of energy for graphite of 5.0 kJ mol^{-1} (carbon atom)$^{-1}$. Recently, Totton et al. [34] used a stochastic basin hopping global optimization scheme to locate low-lying local minima on the potential energy surfaces of molecular clusters of 50 coronene and 50 pyrene molecules with mass densities lower than the bulk values of the pure crystalline PAH structures.

The majority of these studies, however, has analyzed the formation and dissociation of pairs of molecules, and compared the lifetimes of dimers with the characteristic time obtained from chemical growth rate or collision interval to assess the role of dimers as soot nuclei [17–19]. But whether dimers are stable enough to accommodate further growth toward soot nuclei is yet to be determined.

The purpose of this work is to gain insights on the physical interactions of PAH to define their principal nucleation pathways in flames. We, therefore, analyze systems composed of thousands of small aromatics to determine their clustering behavior as function of molecular mass, morphology as well as temperature, using Molecular Dynamics simulations. The results provide critical information for the development of future nucleation model.

2. Methodology

Atomistic Molecular Dynamics (MD) simulations are used to study the formation of clusters of PAH of different masses and morphologies in a wide range of temperatures. The non-bonded interactions of the potential contain a repulsion and a dispersion term expressed as Lennard–Jones (LJ) potential form, in addition to a Coulomb contribution:

$$V_{\text{non-bonded}}(r_{ij}) = 4\varepsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right) + f\frac{q_i q_j}{r_{ij}} \quad (1)$$

where the electric conversion factor is $f = \frac{1}{4\pi\varepsilon_0} = 138.935485(9)$ kJ mol^{-1} nm e^{-2}. The parameters used for the LJ potential are from the work of Miller and co-workers [35]. These potentials have been used to investigate physical coagulation of aromatics in several previous studies on soot nucleation [20,35,36]. The effective atomistic electrostatic potential charges were obtained from the electronic structure calculations using Gaussian 03 program [37] with the B3LYP/6-31G** level of theory [38–40]. For the intramolecular interactions, the OPLSAA [41,42] parameters for bonds, angles, and dihedrals were used. The NVT ensemble was employed for the simulations and the constant temperature was maintained with the Nosé–Hoover thermostatting method [43] with a time constant of 0.03 ps. All calculations were performed using the Gromacs 4.0.3 program package [44] with an integration time step of 1 fs.

3. Results and discussion

As mentioned in the previous section, the goal of this study is to understand the effect of molecular mass, morphology and temperature on the clustering behavior of PAH in order to determine the feasibility of a physical nucleation pathway to describe the transition from small PAH to macromolecular structures. Figure 1 reports the structures of hydrocarbons considered in this study. Besides peri-condensed aromatics (PCAH) such as pyrene (P), coronene (C) and tri-acenaphtri-phenylene (T), (Fig. 1(a–c)), we included peri-condensed aromatics with an aliphatic branch (PCAB) such as 1,2, and 4-vinyl-3a^1,5a^1-dihydropyrenes (VP), and 1-vinylcoronene (VC) (Fig. 1 (d and e)), and aromatic molecules linked by aliphatic chains (AALH) such as 1,2-di(naphthalen-2-yl)ethane (DNE), 1,3-di(naphthalen-2-yl)propane (DNP), 2-(2-(1,9-dihydropyren-2-yl)ethyl)pyrene (DEP), and 2-(3-(1,9-dihydropyren-2-yl)-propyl)pyrene (DPP) (Fig. 1(f–i)).

Molecular Dynamics simulations of homo-molecular and hetero-molecular systems composed of 1000 molecules were carried out at four temperatures – 500 K, 750 K, 1000 K, and 1500 K. In our calculations we assumed that the majority of the collisions were bi-molecular and there was a random distribution of collisions between molecules

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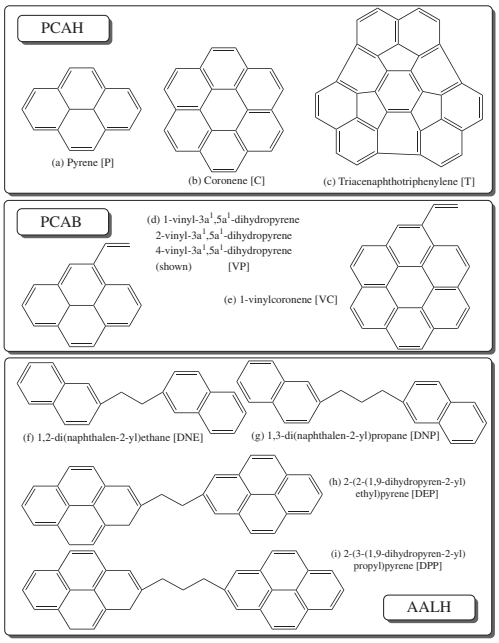


Fig. 1. Pool of molecules identified for this study.

[45]. This assumption was supported by the fact that the density of the systems simulated (2×10^{18} cm^{-3}) was lower than the density of an ideal gas in the same conditions of temperature and pressure, implying that the occurrence of a collision does not affect the likelihood of a subsequent collision. In this context, the collision efficiency is independent of the system density, and the time scale in MD simulations can be related to the time in flames using the following relation:

$$\frac{(n_{\mathrm{MD}})^2\pi(b_{\mathrm{coll,MD}})^2\bar{v}_{\mathrm{MD}}}{(n_{\mathrm{Flame}})^2\pi(b_{\mathrm{coll,Flame}})^2\bar{v}_{\mathrm{Flame}}} = \frac{\Delta t_{\mathrm{Flame}}}{\Delta t_{\mathrm{MD}}} \tag{2}$$

where n is the concentration of molecules, b_{coll} is the collision diameter, and $\bar{v}$ is the average velocity. Since the collision diameters b_{coll} for the molecules analyzed with MD and the ones in the flame environment are the same, as well are the temperatures of the two systems, then the average velocities of the particles $\bar{v}_{\mathrm{MD}}$ and $\bar{v}_{\mathrm{Flame}}$ are equivalent and:

$$\Delta t_{\mathrm{Flame}} \simeq \Delta t_{\mathrm{MD}} \times \left(\frac{n_{\mathrm{MD}}}{n_{\mathrm{Flame}}}\right)^2 \tag{3}$$

This important relationship has been validated in our previous study [36] showing a very good agreement between simulation results and theoretical predictions. Based on Eq. (3), if the number density of the aromatics in flame is ca. 1×10^{15} cm^{-3} [7], 1 ns of MD simulation time corresponds to 8.5 ms in flame. Therefore, in this study, a simulation time of 1 ns is used for all the computations, assuming that it provides enough time for soot nucleation [36].

One of the important criteria in this study is the definition of cluster. To this end, we used two conditions: (i) a molecule should be within 1.5 nm distance of another molecule; and (ii) condition (i) should be satisfied for at least 10 ps, since the proximity of molecules alone can not rule out mere collision events. The 1.5 nm cutoff seems to be an arbitrary selection, but it does not significantly influence the result, and the 10 ps lifetime cutoff is the most critical factor that should be satisfied.

3.1. Systems of molecules of similar masses

Figure 2 reports the percentage of molecules in the form of clusters for the homo-molecular PCAB and AALH systems, together with the size of maximum cluster. At low temperatures we observed the formation of clusters in all the systems analyzed. This process is highly dependent on the masses of the molecules. For example, at 500 K and 750 K, differently from C (300 amu) and T (444 amu), P (202 amu) does not show a significant formation of clusters. The different behavior of P as compared with C and T is in agreement with the study reported by Grotheer and co-workers [46], who determined the mass range of dimers in flames to be between 675 amu and 900 amu. These values of molecular weights are similar to the ones of C and T dimers, but higher than the molecular weight of P dimers. An interesting aspect of the clustering behavior at high temperatures, such as 1000 K and 1500 K, is the maximum size of clusters, is the predominant presence of dimers and trimers. This phenomenon can be understood in terms of the total number of effective collisions during the 1 ns simulation time as shown in Fig. 3. The light grey bars show the number of effective collision events, defined as collision leading to clusters, at different temperatures. This value is influenced by either low collision frequency due to high cluster efficiency at low temperature or low collision efficiency at high temperature. The patterned dark gray bars indicate the number of effective collisions that survived for the entire simulation time without undergoing dissociation. At 500 K and 750 K, even though the majority of clusters dissociate during the simulations, a significant number of effective collisions survive until the end of the simulations, which indicates the formation of nuclei. At high temperatures, the opposite behavior was identified, suggesting that cluster formation is very unstable and at the same time a highly reversible process. The combination of high number of effective collisions and the fact that most of clusters dissociated, result in an almost constant value of the maximum cluster size at high

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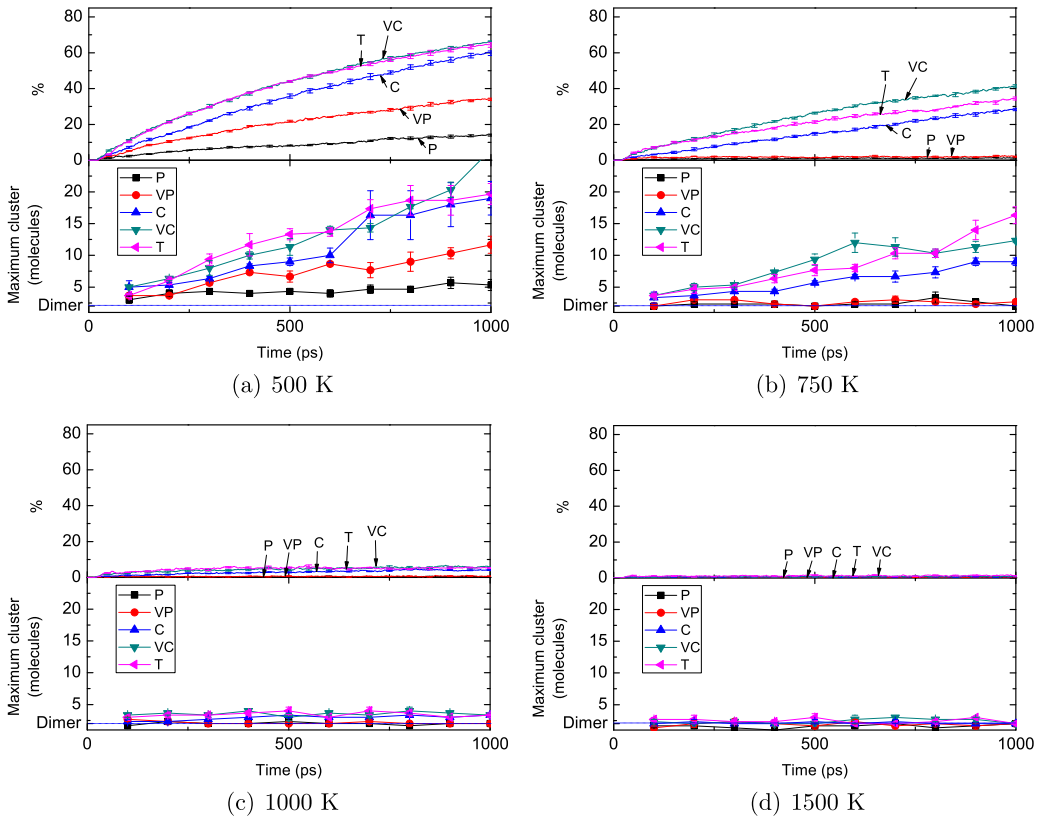


Fig. 2. Percentage of molecules in the form of clusters (upper graphs) and maximum cluster size for homo-molecular systems of P, C, T, VP, and VC at four temperatures. The values of maximum cluster size were sampled at 100 ps intervals.

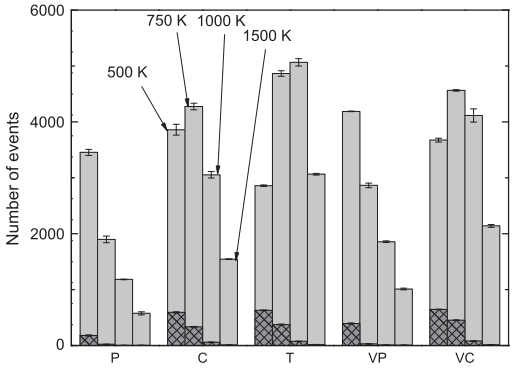


Fig. 3. Number of effective collisions leading to the formation of clusters for five systems as function of temperature. Patterned dark gray bars indicate the number of events that lasted until the end of the simulation time.

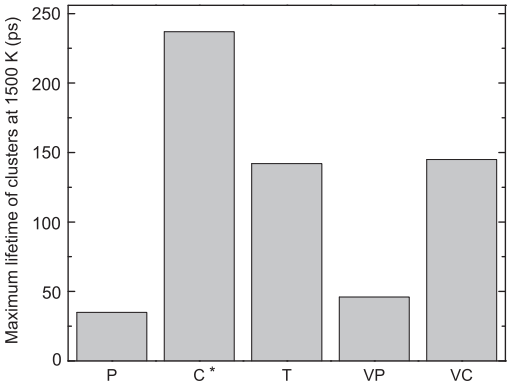


Fig. 4. Maximum lifetimes of clusters at 1500 K for P, C, T, VP and VC. The clusters dissociated during the simulations except for coronene.

temperatures as reported in Fig. 2. Even if the lifetimes of dimers and trimers formed is substantially long, as reported in Fig. 4, reaching 30 ps for P and VP molecules and 100–200 ps for C, VC and T, the results reported in Fig. 2(c and d) clearly show that they do not act as nuclei for bigger particles. The maximum lifetimes reported in this paper are longer than the predictions obtained from previous studies on dimer forma-

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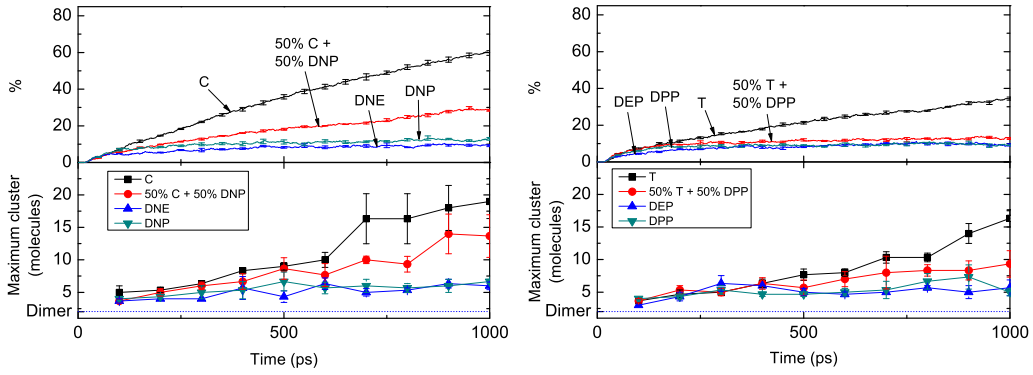
tion by molecular pair collisions [18,17]. However, the results of our simulations imply that the lifetime of a dimer alone may not be used to define the nucleation process, since it does not guarantee that a cluster will be the seed for a large scale nucleation process.

The results reported in Figs. 2 and 3 show that the morphology of aromatic molecules is another important factor that affects the nucleation process. These types of structures have been selected for this study because of their similarity to the intermediates of the HACA process. The inclusion of an aliphatic chain in the structure of the molecules, for example for VC and VP, as compared with C and P, enhances the clustering behavior. VP and VC show higher percentages of clustered molecules, larger maximum size of clusters, and more effective collisions. VC, also, displays a higher percentage of clusters than T, despite the fact that the atomic mass of T is 36% heavier than that of VC. Clusters formed with PCAB (VC and VP) and PCAH (C, P and T) molecules show similar stacking configurations. Inspection of the cluster configurations did not show any repetitive pattern caused by the presence of the aliphatic chains. This result suggests that the higher number of clusters for the PCAB systems is not due to the bigger number of interaction sites because of the presence of the aliphatic chains. In addition to PCAB and PCAH systems, we also studied the behavior of AALH molecules. Figure 5 shows the percentage of clusters and maximum number of cluster for PCAH systems (molecules C and T) and AALH (molecules DNE, DNP, DEP and DPP). Homo-molecular systems of AALH molecules form less and smaller clusters than PCAH systems. To better understand the effect of molecular shape on clustering, we simulated hetero-molecular systems of PCAH and AALH with similar masses (50% C (300.35 amu)–50% DNP (296.40 amu), and 50% T (444.48 amu)–50% DPP (446.58 amu)). These systems show an intermediate behavior, having a faster nucleation rate than AALH but slower than homo-molecular PCAH. This result is in agreement with the work reported by Wong et al. [18], who studied bi-collisions of AALH dimers using Molecular Dynamics and reported a substantially lower lifetimes for AALH than the PCAH of comparable masses.

In summary, the morphology of molecules is highly related to the nucleation process. Among the systems studied, PCAB have the fastest clustering behavior and AALH the slowest. These results suggest the potential role of PCAB molecules as precursors of macromolecular structures via a physical nucleation process. Since these molecules are similar to the intermediates of the HACA growth model, we can infer that these compounds can also contribute to the growth of carbonaceous macromolecules via a physical nucleation process in specific ranges of temperatures.

3.2. Systems of molecules of different masses

So far, we have considered systems composed of molecules with the same mass or similar masses. In flame environments, however, particle nucleation is characterized by a distribution of molecules with different sizes [7]. To understand the effect of molecular masses on nucleation, homo-molecular systems of P, C, and T reported in Fig. 2 were seeded with 1% fullerene molecules C_{60} and C_{180}. This value was chosen to minimize the effect on average molecule size. The results show that fullerenes have a limited effect on the maximum size of cluster, as reported in Fig. 7. Their main role is to increase the size of maximum



(a) 500 K (b) 750 K

Fig. 5. Percentage of molecules in cluster (upper graphs) and maximum cluster size for (a) homo-molecular systems of C, DNE, and DNP and hetero-molecular systems of 50% C–50% DNP at 500 K; homo-molecular systems of T, DEP, and DPP, and hetero-molecular systems of 50% T–50% DPP at 750 K. Maximum cluster size data were sampled at 100 ps intervals.

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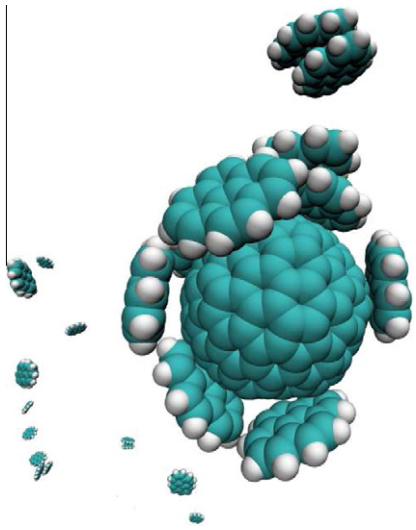
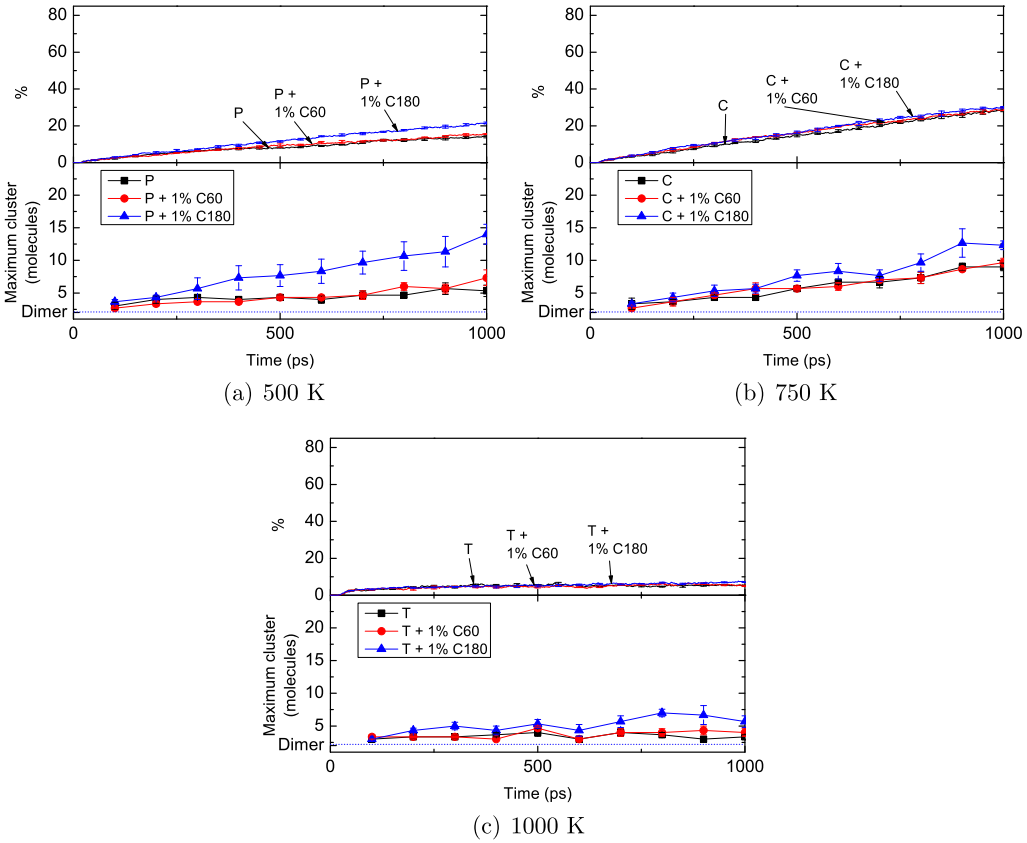


Fig. 6. C_{180} fullerene surrounded by a layer of coronene molecules.

cluster by acting as core nuclei for small PAH molecules as shown in Fig. 6. The results are in agreement with the findings reported by Ishiguro et al. [47] using high resolution transmission electron microscopy, who showed the formation of structures similar to the ones reported in Fig. 6 with an inner core composed of spherical fine particles surrounded by an outer shell of graphitic structures. The first layer of PAH around the surface of fullerenes is observed in most of the MD simulations, while a second or third layer of PAHs is only detected at low temperatures. Difficulties in forming the second layer may also indicate the need for chemical bonding between molecules in the same layer level or adjacent layers. The inclusion of larger fullerene molecules, however, does not have a strong influence on the percentage of molecules in clusters.

In order to relate the MD findings with soot and nanoparticle formation models, we determined the collision efficiency of PAH and the results are displayed in Fig. 8. The computed values are higher than those obtained experimentally by D'Alessio and co-workers for particles with the same diameters [48]. However, at 1500 K, the collision efficiencies are in good agreement with the collision efficiencies for



(a) 500 K

(b) 750 K

(c) 1000 K

Fig. 7. Percentage of molecules in cluster (upper graphs) and maximum cluster size for (a) homo-molecular systems of P, hetero-molecular systems of 99% P–1% C_{60}, and 99% P–1% C_{180} at 500 K; (b) homo-molecular systems of C, hetero-molecular systems of 99% T–1% C_{60} and 99% T–1% C_{180} at 1000 K.

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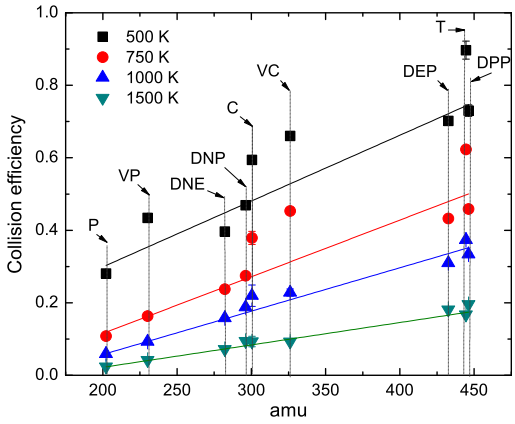


Fig. 8. Collision efficiencies as function of temperature and molecular weights for the aromatics reported in Fig. 1. Each temperature data were linearly fitted.

PCAH molecules obtained by Kraft and co-workers [49]. Interestingly, PCAB type molecule, such as VC, has lower collision efficiency than T but faster nucleation rate as shown in Fig. 2. One possible explanation is the important role of chains, since PCAB molecules can accommodate the collision energy in additional internal degrees of freedom stabilizing the cluster after the effective collision, rather than having higher collision efficiency.

4. Conclusions

In this paper we studied the formation of homo- and hetero-molecular PAH clusters in a wide range of temperatures and analyzed the implications for the soot nucleation process. The main trend is cluster formation with an increase in molecular mass and a decrease in temperature. Between 1000 K and 1500 K, which are typical flame temperatures for soot nucleation, we observed the formation of small PAH clusters (2–5 molecules) with maximum lifetimes ranging between 10 ps or 240 ps. However, these clusters are not stable enough to accommodate the further growth into larger particle. This result raises doubts regarding the ability of these clusters to act as soot nuclei.

The morphology of hydrocarbons is another important parameter for the nucleation process and the Molecular Dynamics results reported in this paper show that aromatics with an aliphatic chain (PCAB), which can be formed via HACA-like mechanism, have a faster nucleation rate than peri-condensed aromatics (PCAH) and aromatic molecules linked by aliphatic chains (AALH) with comparable masses. AALH type molecules show the slowest nucleation rate.

The collision efficiencies for the different systems were determined as a function of temperatures. Similar collision efficiencies between molecules in the PCAB and PCAH systems may imply that the aliphatic chain attached to PAH does not increase the collision efficiency, but enhances the ability of molecules to accommodate energy after the collision because of the added internal degrees of freedom.

The importance of particle size distribution during the nucleation process was studied by seeding the systems of small aromatics with fullerenes. The MD results show that the main effect of fullerenes is to increase the maximum cluster size by acting as core nuclei for small PAH molecules as shown in Fig. 6.

In terms of soot modeling, the results reported in this paper can provide critical information for the development of a more complex nucleation model that include physical and chemical growth mechanisms. Specifically, the results provide information on the mass and temperature ranges for a physical nucleation process. In addition, the morphology of molecules plays an important role in the nucleation rate and molecules with an aromatic core and aliphatic chains show higher nucleation rates than the corresponding aromatic molecules without chains. This result suggests the important role of the chains as a sink to accommodate the collision energy, facilitating the growth of clusters.

In conclusion, aliphatic chains attached to aromatic sites can facilitate the growth of clusters, and the physical nucleation is viable in the temperature range up to 750 K for the systems reported in this study. For temperatures higher than 1000 K, another mechanism needs to be invoked for the formation of clusters such as the chemical bonding between molecules in a cluster. This topic will be the subject of our future study.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.proci.2010.06.038.

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