Temperature evolution, atomistic hot-spot effects and thermal runaway during microwave heating of polyacrylonitrile: A ReaxFF molecular dynamics simulation

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\begin{abstract}
Microwave is of promising applications in various chemical and material processes, however, the interactions between the microwave and the molecules from atomistic scales are lack of understanding. ReaxFF reactive molecular dynamics simulations were carried out to get insights into the interactions between the microwave and polyacrylonitrile (PAN) during microwave heating. It was found that the temperature evolution of the system was dependent on the electric field strength and frequency of the microwave. The alternate change of the electric field of the microwave lead to the alternate fluctuation of the temperature. We surprisingly predicted the atomistic hot-spot effect of microwave heating of PAN that the cyano groups were selectively heated. With an electric field intensity of 0.6 V Å\textsuperscript{-1} and a frequency of 60 GHz, the temperature of the hot-spot atoms was 300 and 500 K higher than the carbon and hydrogen atoms in the PAN backbone, respectively. We also analyzed the thermal runaway behavior of the system during microwave irradiations and found that it was attributed to the decomposition of PAN into smaller polar molecules. This work suggests that it is possible to selectively and effectively activate the cyano groups of PAN to improve their reactivity.
\end{abstract}

\textbf{KEYWORDS}
copolymers, irradiation, theory and modeling, thermal properties

\section{INTRODUCTION}
Microwaves have been widely used in everyday cooking and satellite communications. In industry, microwaves have been employed to accelerate chemical reactions after the commercialization of microwave ovens in the 1950s.\textsuperscript{[1,2]} In 1986, Gedye et al.\textsuperscript{[3]} carried out experiments of nucleophilic substitution, high-temperature oxidation, and hydrolysis of organic compounds, and add reactions with microwave heating. It was found that microwave irradiations could greatly enhance the reactivity and productivity of some chemical reactions.\textsuperscript{[3-5]}

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Ricciardi et al. [6] reported that microwave heating could give 7–13 times higher first-order rate constants for the xylose dehydration reaction than traditional heating. This result was attributed to the local overheating of xylose under microwave irradiation. Sonker et al. [7] prepared cross-linked PVA films by conventional heating (hot-air oven) and microwave irradiation. They found that the cross-linking time using a microwave was about one-eighth of that with the conventional (hot-air oven) approach, however, the obtained materials with the two methods had the same water absorption, tensile strength, and thermal stability. Shi et al. [8] prepared octenyl succinic anhydride-modified starch by microwave irradiation in an aqueous medium and found that microwave irradiation could reduce both the activation energy of the reaction and the pre-exponential factor. More recently, researchers have been encouraging the application of microwaves in organic synthesis and flow chemistry. [9–13]

One of the promising applications of microwaves is to accelerate the oxidation reactions in the thermal stabilization process of carbon fiber production. Polycrylonitrile (PAN) is one of the most widely used precursors of carbon fibers, and the corresponding carbon fibers account for more than 90% of their total production. In the production of PAN-based carbon fibers, thermal stabilization is the most critical process, and typically costs about 80 minutes, which takes up 90% of the production time. [14, 15] Such a long time not only results in low efficiency but also large energy consumption. [16] In addition, with the conventional heating method, the nonuniform thermal field in the PAN fiber may cause serious skin-core structure and affect the performance of the final carbon fiber. [17] Most recently, efforts have been devoted to making use of the microwave for the thermal stabilization of PAN precursors to avoid these problems. [18–21]

To make full use of the advantages of microwave irradiations in the thermal stabilization of PAN, we need to make clear the physical picture of the interactions between the microwave and PAN. In recent years, a few molecular dynamics simulations have been done to understand the effects of microwave irradiations on relatively simple systems, such as pure water or aqueous solutions. [22–26] Most of these works did not involve the chemical reaction in the process. So far, there are indeed a few theoretical research focused on microwave chemistry, however, most of them are from a macroscopic scale, [27–29] which is difficult to obtain the details of the process. Therefore, there is a great demand to get insights into the microwave irradiation of PAN and to enhance the fundamental understanding of it.

Here we carried out reactive molecular dynamic simulations to get insights into the process of microwave heating of PAN. We analyzed the temperature evolution of the PAN system and the fragments during microwave heating and report the atomistic hot-spot effects and thermal runaway behavior of the system in the process.

## 2 | MODEL AND SIMULATION DETAILS

The simulation system consists of six PAN chains with a length of 53 monomers. The PAN chains were modeled with the ReaxFF force field, which is developed by van Duin et al. [30] It is based on bond orders and can describe the dissociation and formation of chemical bonds. Because the parameters of the ReaxFF force field were trained from the quantum calculations, it bridges the scales of electrons and atoms, which provides the possibility to involve the interplay between chemical reactions and molecular dynamics in one system. In the ReaxFF force field, the system energy is the sum of several partial energy contributions as follows [30, 31]:

\[
E_{\text{sys}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{tor}} + E_{\text{conj}} + E_{\text{vd}} + E_{\text{coul}}
\]

where \(E_{\text{bond}}\) is the bond energy associated with chemical bonds between atoms and is a function of interatomic distance, \(E_{\text{over}}\) and \(E_{\text{under}}\) are energy penalties imposed for over-coordinated atoms and under-coordinated atoms based on atomic valence rules, \(E_{\text{val}}\) and \(E_{\text{tor}}\) are the valence angle energy and torsion angle energy, \(E_{\text{conj}}\) is the contribution of conjugation effects to the molecular energy, \(E_{\text{vd}}\) is the energy of the van der Waals interactions and \(E_{\text{coul}}\) is the energy of coulombic interactions.

Microwave refers to electromagnetic waves with a frequency of 300 MHz to 300 GHz, including electric and magnetic fields. Since the system involved is nonmagnetic, it is only necessary to consider the effect of the electric field on the system during microwave irradiations. [22] At the same time, the wavelength of the microwave (\(\lambda > 1\) mm) is much larger than the size of the molecular dynamics simulation system (\(<1\) nm). Therefore, the instantaneous electric field of the system can be treated as a uniform distribution over the whole frequency range of the microwave. According to the analysis by Kumar et al., [32] the energy of the microwave photon is very low in practical situations, which cannot damage the chemical bonds directly, but leads to the heating of the system. The electric field associated with the microwave can be expressed as follows [22, 23]:

\[
\vec{E} = \vec{e}_n E_0 \cos(2\pi f t)
\]

where \(E_0\) and \(\vec{e}_n\) are the amplitude and direction of the electronic field, and \(f\) and \(t\) are the frequency of microwave and time, respectively.
All the simulations were performed with the LAMMPS package. The initial size of the simulation system is $100 \times 100 \times 100\text{Å}$. Before the simulation of the microwave irradiation process, the system was equilibrated with the Optimized Potentials for Liquid Simulations (OPLS) forcefield. First, energy minimization of the system was evaluated, and the system was relaxed at 1000 K with a constant atom number, constant pressure, and constant temperature (NPT) ensemble for 100 ps. When the NPT simulation is done, several annealing runs with an NPT ensemble were performed to accelerate the equilibration of the system, including 300 to 1000 K in 100 ps, 1000 K for 100 ps, 1000 to 300 K in 100 ps, and 300 K for 100 ps. Then the simulation run at 300 K was carried out in a canonical ensemble. Finally, the system reached the equilibrium size of $15.41\times 15.41\times 15.41\text{Å}$ with a density of 0.932 g cm$^{-3}$. In this stage, the timestep is 1.0 fs. After the system was equilibrated in the OPLS force field, it was alternated to the ReaxFF force field to simulate the microwave heating process. Microwave frequencies of 20-100 GHz and electric field amplitudes of 0.2-1.0 V Å$^{-1}$ were considered. The timestep is 0.1 fs.

3 | RESULTS AND DISCUSSION

3.1 | Temperature evolution

The simulation was carried out for the microwave heating process of PAN with a frequency of 60 GHz and an electric field amplitude of 0.6 V Å$^{-1}$. The temperature evolution of the simulated system is shown in Figure 1. The temperature curves can be divided into two phases, and they can be fitted separately with the equation:

$$T(t) = \begin{cases} 
4000 - 3700e^{-t/144.235} & T \leq 2000\text{K} \\
1900 + 100e^{(t-88.6252)/25.4412} & T > 2000\text{K} 
\end{cases} \quad (3)$$

where $T(t)$ is the system temperature in K, $t$ is the simulation time in ps. As shown in Figure 1, the system temperature exhibits periodic vibration over time. This observation is due to the periodical change of the external electric field of the microwave. The curve shows that the growth rate of temperature is nearly constant under 2000 K. When the temperature is above 2000 K, it increases exponentially. Such an abrupt rise in temperature caused by microwave irradiations is called “thermal runaway” here. Such a phenomenon was also reported with the temperature evolution of poly(vinyl chloride) during microwave heating by Michałowski et al. This phenomenon is attributed to the generation of a lot of small polar molecules above 2000 K from the pyrolysis reaction of PAN, since the polar fragments have good absorption of microwaves.

3.2 | Influences of microwave frequency and electric field strength on heating characteristics

The frequency and electric field strength of microwaves have an important influence on the heating process. The temperature evolution of PAN during microwave irradiation for the electric field strength of 0.2-1.0 V Å$^{-1}$ is shown in Figure 2. It can be seen from Figure 2 that the heating rate increases nonlinearly with the electric field strength. The fluctuation of temperature also increases with the electric field strength. It is found that the five curves meet
the following equation$^{[37]}$:

$$T(t) = 4000 - 3700 \cdot e^{-t/\beta} \quad (4)$$

where \(T(t)\) is the system temperature in K, \(t\) is simulation time in ps, and \(\beta\) is the correlation coefficient.

To explore the dependence of \(\beta\) on the frequency and electric field strength of the microwave, simulations of PAN heated by microwave irradiation were carried out in the frequency range of 20\(\sim\)100 GHz and the electric field amplitude of 0.2-1 V Å\(^{-1}\). The obtained results are shown in Figure 3. With the temperature evolution of these systems, we found that the dependence of \(\beta\) on the frequency and electric field strength of microwave can be well described as$^{[37]}$:

$$\beta = A f^a + B s^b + C f^a s^b + D \quad (5)$$

where \(f\) and \(s\) are the microwave frequency in GHz and the electric field strength in V Å\(^{-1}\), respectively. \(A, B, C, D, E, F\) are the fitting parameters and their fitted values are listed in Table 1. Therefore, the temperature evolution during the microwave heating of PAN under various frequencies and electric field strengths can be described as$^{[37]}$:

$$\begin{cases} T(t) = 4000 - 3700 \cdot e^{-t/\beta} \\ \beta = A f^a + B s^b + C f^a s^b + D \end{cases} \quad (6)$$

### Table 1 Fitted parameters of Equation (5) and Equation (6)

| Parameter | A     | a    | B     | b    | C    | D    |
|-----------|-------|------|-------|------|------|------|
| Value     | 1542.328 | −1.04177 | 22.87249 | −1.95055 | 1806.583 | −8.31991 |
has the slowest heating rate, as shown in the inset of Figure 4. In the second half of the cycle, the temperature of the nitrogen atom tends to decrease slowly, the temperature of the carbon atom remains essentially constant, and the temperature of the hydrogen atom continues to rise at the same rate as the first half. This phenomenon is because in the first half of the cycle, the electric field of the microwave is strong, and the PAN chains can absorb more microwave energy.

In this process, because the electronegativity of the nitrogen atom is stronger than the hydrogen and carbon atoms, the nitrogen atoms absorb more microwave energy. So in the first half of the cycle, the temperature of the nitrogen atom is higher than that of the other elements of atoms. In the second half of the cycle, the electric field strength of the microwave is weakened, and the microwave energy absorbed by the PAN molecular chains is gradually reduced. Because the nitrogen atom absorbed more energy, and its temperature is higher in the first stage, the motion of the nitrogen atom is more intense. The collision between nitrogen atoms and adjacent carbon, hydrogen atoms is more intense, and the energy is transferred from the nitrogen atom to the carbon and hydrogen atoms, causing the temperature of the carbon and hydrogen atoms to rise. However, because the temperature of the carbon atom is higher than that of the hydrogen atom, the energy of the carbon atom is also partially transferred to the hydrogen atom. At this stage, the energy absorbed by the carbon atom from the nitrogen atom is approximately equal to the energy transmitted to the hydrogen atom, so the temperature of the carbon atoms remains substantially constant while the temperature of the nitrogen atom decreases and the temperature of the hydrogen atoms continue to rise at a constant rate.

To determine the difference of temperature evolution between the side groups and the backbone, we calculated the temperature of the backbone and the side groups, respectively in Figure 5. In the early stage of microwave heating, the temperature of the side cyanogroups is higher than the backbone, which consists of carbon and hydrogen atoms. When the microwave heating time is 8.5 ps, the temperature difference between the backbone and the branch reaches the maximum, 150 K. At this point, the temperature curve of the cyanogroups just reaches the second peak. As the microwave heating time increases, the cyanogroups absorb more energy than the backbone due to their larger polarity. Therefore, the temperature difference between the side groups and the backbone at the second peak is larger than that at the first peak. However, as the temperature increases, the collision and energy transfer between the cyanogroups and backbone atoms also increases, resulting in the decrease of the temperature difference between the cyanogroups and the backbone from the third peak. The temperature difference between the branch and the backbone also decreases as the temperature increases. When the temperature reaches 1400 K, the temperatures of the cyanogroups and the backbone tend to be the same.

The above results suggest that there are atomistic hot-spot effects with the PAN during microwave heating. To clearly show the details of hot-spot atoms, we calculated the temperature distribution over the atoms in the simulation system. The temperature was obtained by average the atom temperature over 100 frames in 0.1 ps.

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involved in chemical reactions. In addition, it is also possible to tune the melting behavior of PAN by microwave irradiation.

### 3.4 Thermal runaway behavior of microwave irradiated PAN

To explore the reasons for the thermal runaway of PAN above 2000 K, the systems were heated by microwave irradiation and gradually elevating the temperature for comparison (namely traditional heating), respectively. The simulations in this part were divided into two stages. The first part is the rapid heating stage. The system is quickly heated to 2000 K by high-intensity microwaves. In this stage, a microwave with a frequency of 100 GHz and an electric field intensity of 2.7 V Å\(^{-1}\) was used as the heating source to heat the system to 2000 K in 10 ps with a timestep of 0.1 fs. In the second stage process, keeping the frequency of the microwave constant, the electric field intensity of the microwave is decreased to 0.03 V Å\(^{-1}\), and the heating period is 500 ps with a timestep of 0.1 fs. For the convenience of comparison, the procedure for the traditional heating of PAN was the same as that of microwave heating.

The temperature evolution of the systems heated by traditional methods and microwave irradiation is shown in Figure 7A-B. It can be seen from the figure that in the system with the traditional heating method, the temperature is of equilibrium at the set value, while it is out of control under microwave irradiation. We checked the microstructures of the two kinds of systems in the first heating stage by their pairwise radial distribution functions, and it is revealed that there is little difference between the microstructures. Therefore, the thermal runaway of the system is not associated with the first rapid heating process.

We also calculated the number evolution of acrylonitrile, hydrogen cyanide, hydrogen, and other small polar molecules for the systems heated by traditional method and microwave irradiation, shown in Figure 7A-B. The figure reveals that PAN decomposes more rapidly in the system of microwave irradiation than in the traditional heated system. The time of producing \(\text{H}_2\) in the traditional heated system is much earlier than that in the microwave irradiation one, and the amount of \(\text{H}_2\) increases linearly with time. However, the amount of produced hydrogen and other small polar molecules increases exponentially. This is because acrylonitrile molecules have larger dipole moments and are easier to be activated to decompose into small molecules. These small polar molecules have larger absorption ability and thermal conversion coefficients of the microwave because there are fewer bond constraints on them than on the PAN chains. These two properties contribute to the thermal runaway of the microwave irradiated system.

### 4 Conclusion

In this work, the simulation of microwave heating of PAN by ReaxFF molecular dynamics simulations was carried out and the characteristics of temperature evolution were analyzed. It is found that the temperature evolution of the system is strongly dependent not only on the electric field strengths of the microwave but also on its frequency. The alternate change of the electric field of the microwave leads to the alternate fluctuation of the temperature. From the simulation, we predicted the atomistic hot-spot effect of microwave heating of PAN where the cyano groups are selectively heated. With the considered power of microwave irradiation, the temperature difference between the hot-spots and the carbon atoms in the PAN backbone is as high as about 300 K, and that between the hot-spots and the hydrogen atoms is even as high as about 500 K. We also analyzed the thermal
runaway behavior of the system heated by microwave irradiations. By comparison with the system gradually heated by the traditional method, we found that the thermal runaway of the system is attributed to the decomposition of PAN into smaller polar molecules, which have better microwave absorption and thermal conversion efficiency. This work suggests that it is possible to selectively and effectively activate the cyano groups of PAN chains for pre-oxidation during their thermal stabilization. Our future work will be focused on the microwave pre-oxidation of PAN.

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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REFERENCES
1. A. David, Nature 2003, 421, 571.
2. C. O. Kappe, Angew. Chem., Int. Ed. 2010, 43, 6250.
3. R. Gedye, F. Smith, K. Westaway, H. Ali, L. Baldisera, L. Laberge, J. Rousseau, Tetrahedron Lett. 1986, 27, 279.
4. Y. Wada, S. Tsubaki, M. M. Maitani, S. Fujii, F. Kishimoto, N. Haneishi, J. Jpn. Pet. Inst. 2019, 58, 14273.
5. E. Ahmad, M. I. Alam, K. K. Pant, M. A. Haider, Ind. Eng. Chem. Res. 2019, 58, 16055.
6. L. Ricciardi, W. Verboom, J.-P. Lange, J. Huskens, ACS Sustain. Chem. Eng. 2019, 7, 14273.
7. A. K. Sonker, V. Verma, J. Appl. Polym. Sci. 2018, 135, 46125.
8. H. Shi, Y. Yin, A. Wang, L. Fang, S. Jiao, J. Appl. Polym. Sci. 2016, 133, 43909.
9. G. B. Dudley, A. E. Stiegmier, Chem. Rec. 2017, 18, 381.
10. R. Nagahata, K. Takeuchi, Chem. Rec. 2019, 19, 51.
11. J. Xi, Z. Yu, J. Appl. Polym. Sci. 2018, 135, 45767.
12. Á. Díaz-Ortiz, P. Prieto, A. de la Hoz, The Chemical Record 2019, 19, 85.
13. Y. Monguchi, T. Ichikawa, T. Yamada, Y. Sawama, H. Sajiki, Chem. Rec. 2019, 19, 1.
14. S. Y. Kim, S. Lee, S. Park, S. M. Jo, H. S. Lee, H. I. Joh, Carbon 2015, 94, 412.
15. W. Zhang, M. Wang, W. Zhang, W. Liu, C. Yang, R. Shen, G. Wu, Polym. Degrad. Stab. 2018, 158, 72.
16. G. Golkarnarenjil, M. Naebe, K. Badli, A. S. Milani, R. N. Jazar, H. Khayyam, Materials 2018, 11, 13.
17. S. Nunna, C. Creighton, B. L. Fox, M. Naebe, M. Maghe, M. J. Tobin, K. Bambery, J. Vongsivivut, N. Hameed, J. Mater. Chem. A 2017, 5, 7372.
18. Z. Cheng, J. Liu, S. Guo, S. Xiao, Z. Shen, X. Lei, Ceram. Int. 2018, 44, 14377.
19. T. H. H. Elagib, E. A. M. Hassan, C. Fan, K. Han, M. Yu, Polym Eng Sci. 2019, 59, 457.
20. T. H. H. Elagib, E. A. M. Hassan, B. H. Liu, K. Q. Han, M. H. Yu, Carbon Lett. 2020, 30, 235.
21. T. H. H. Elagib, E. A. M. Hassan, C. Fan, K. Han, M. Yu, Polym. Degrad. Stab. 2018, 158, 64.
22. N. J. English, J. M. D. MacElroy, J. Chem. Phys. 2003, 118, 1589.
23. T. Mohoric, U. Bren, J. Mol. Liq. 2018, 266, 218.
24. Y. Tasei, B. Mijiddorj, T. Fujito, I. Kawamura, K. Ueda, A. Naito, J. Phys. Chem. B 2020, 124, 9615.
25. Y. Hu, G. Jia, J. Mol. Liq. 2020, 297, 111440.
26. X. Yang, K. Cheng, G.-z. Jia, Mol. Phys. 2020, 118, e1662505.
27. X. Zhang, Z. Zhao, C. Wang, Adv. Mater. Res. 2014, 838–841, 1898.
28. W. Wang, Z. Ma, X. Zhao, S. Liu, L. Cai, S. Q. Shi, Y. Ni, ACS Sustain. Chem. Eng. 2020, 8, 16086.
29. M. Keramat, M.-T. Golmankani, E. Durand, P. Villeneuve, S. M. H. Hosseini, J. Chem. Technol. Biotechnol. 2021, 96, 704.
30. A. C. T. van Duin, S. Dasgupta, F. Lorant, W. A. Goddard, J. Phys. Chem. A 2001, 105, 9396.
31. K. Chenoweth, A. C. T. van Duin, W. A. Goddard, The Journal of Physical Chemistry A 2008, 112, 1040.
32. A. Kumar, Y. Kuang, Z. Liang, X. Sun, Mater Today Nano 2020, 11, 100076.
33. S. Plimpton, J Comput Phys 1995, 117, 1.
34. M. Chaimovich, A. Chaimovich, J. Chem. Theory Comput. 2021, 17, 1045.
35. L. W. Jorgensen, S. D. Maxwell, J. Am. Chem. Soc. 1996, 118, 11225.
36. A. Goonie, J. Phys. Chem. B 2021, 125, 937.
37. Y.-M. Zhang, J.-L. Li, J.-F. Wang, B.-Z. Wang In Molecular Dynamics Simulation on Temperature Characteristics of Microwave-Heating NaCl Solution (In Chinese), 2013 National Microwave and Millimeter Wave Conference, Chongqing, China, May 21, Chinese Institute of Electronics: Chongqing, China, pp1674.
38. S. Moriwaki, M. Machida, H. Tatsumoto, M. Kuga, T. Ogura, J. Anal. Appl. Pyrolysis 2006, 76, 238.
39. S. Michalowski, A. Prociak, S. Zajchowski, J. Tomaszewska, J. Mirowski, Polym. Test. 2017, 64, 229.
40. G. A. Kouzaev, Mol. Phys. 2020, 118, e1685691.

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