

A computational probe into dissolution inhibition effects of diazonaphthoquinone photoactive compounds on positive tone photosensitive polyimides

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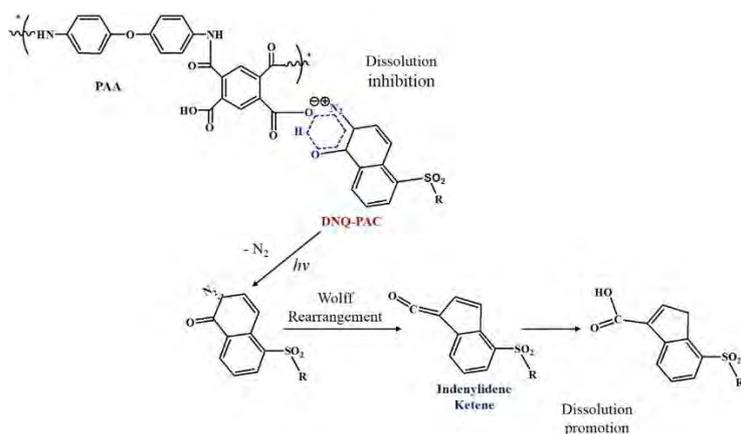
Abstract

Multiscale molecular modeling was performed to evaluate the possible inhibition effects of diazonaphthoquinone photoactive compounds (DNQ PACs) on positive tone photosensitive polyimides (*p*-PSPIs). The density functional theory (DFT) was used to predict the dipole moment of the structures of candidate DNQ PAC models and their corresponding indenylidene ketene (IK) compounds after photolysis reactions. The computed dipole moment increased largely for most IK compounds compared to their original structures, indicating the hydrophobic property of PACs was reduced upon UV irradiation. Seven DNQ PAC-loaded *p*-PSPI films were constructed *in silico* using the Accelrys Materials studio software. Screening and evaluation of the optimal PAC was based on the molecular dynamics simulations of the total interaction energy (E_T), kinetic energy (E_K), solubility parameters (S), cohesive energy density (CED) and Flory-Huggins parameter (χ_{AB}). The obtained results showed that the PACs containing mono functional phenols (type III PACs) had large difference between χ_{AB} values before and after UV exposure, and tended to form a “skin layer” by covering high concentration of PAC on the surface of the corresponding suppositional films. Succinctly, this work demonstrated the applicability of atomistic molecular simulations to the screening and evaluation of DNQ PACs and to understand the possible dissolution inhibition mechanisms.

1. Introduction

Photosensitive polyimides (PSPIs) have been greatly contributed to the progress of microelectronics as packing and insulating materials in recent years. Among different types of PSPI, the positive tone PSPIs (*p*-PSPIs) are more desired in the industrial level due to the fact that *p*-PSPIs can avoid swelling which often occurred in negative tone PSPIs, and provide more environmental friendly and safety issues with the using of aqueous alkaline developers. A variety of *p*-PSPIs have been developed with different chemistries¹, in which the *p*-PSPIs composed of PI precursor, poly(amic acid) (PAA), and a diazonaphthoquinone photoactive compound (DNQ PAC) are the most popular ones. Based on the literature, there are two possible inhibition mechanisms have been proposed for *p*-PSPIs. One is the classical novolac-type hydrogen bonding mechanism (**Scheme 1**)². The other is to form a protectable “skin layer” on the surface of the *p*-PSPI films³.

In this study, molecular simulations have been utilized to evaluate the properties of DNQ PACs, and their interactions with PAA polymers. Density functional theory (DFT) calculations were used to predicate the polarity of small model structures of DNQ PACs as shown in **Figure 1**. Taking into account the impact of the complex PAA polymer chain structures, molecular dynamics (MD) simulations were introduced to estimate the interaction energies of DNQ PACs with PAA polymers and their miscibility, as well as the morphology of the suppositional *p*-PSPI films (**Figure 2**). In order to understand the effect of the photochemistry shown in Scheme 1 on the intrinsic behavior of *p*-PSPI films, we also carried out systematical calculations to mimic the exposed model of the films.



Scheme 1. Novolac-type dissolution inhibition mechanism and the photolysis of DNQ.

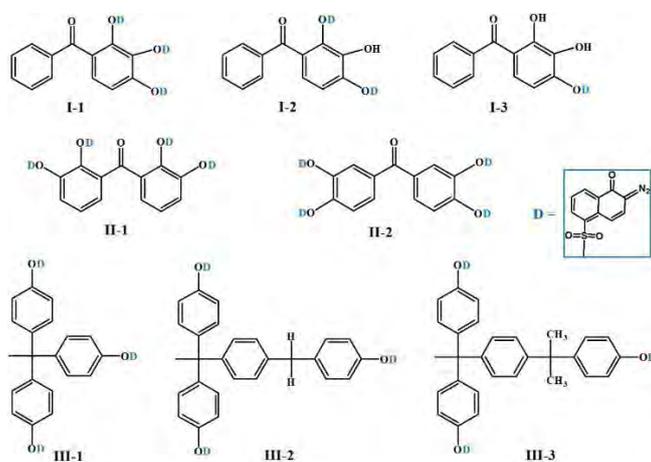


Figure 1. Chemical structures of model DNQ PACs.

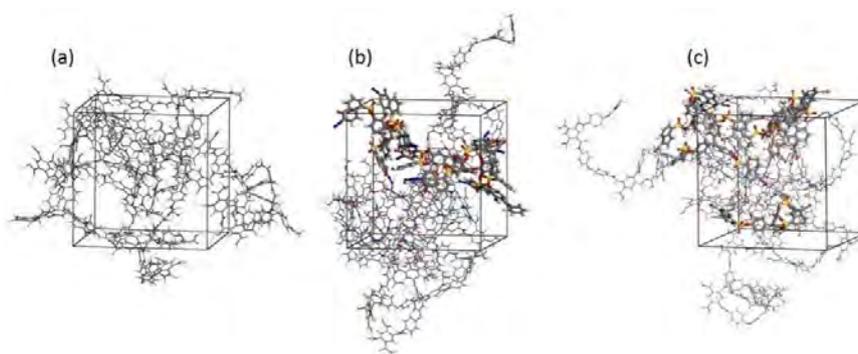


Figure 2. Images of geometrically optimized constructs at the point of convergence: (a) PAA polymer, (b) PF1 before UV exposure, (c) PF1 after UV exposure.

2. Results and discussions

2.1. Prediction of polarity for DNQ-PAC structures and their indenylidene ketone (IK) analogues

In the case of *p*-PSPI development, the photosensitivity and development loss can be determined by the polarity of PAC, and it was found that PACs with small polarity have good dissolution

inhibition³. To estimate the polarity in the DNQ PACs, the dipole moment of the structures was used, whereas a larger dipole moment corresponds to a larger polarity of a compound. DNQ PAC structures given in **Figure 1** were subjected to dipole moment (μ , Debye) calculations after optimization using DFT method on PW91/DNP level, and the obtained results are summarized in **Table 1**.

Table 1. Calculated dipole moment of DNQ_PACs and their indenylidene ketene analogues.

DNQ PAC	Dipol moment (D)	DNQ-IK	Dipol moment (D)
I-1	4.15	I-1	7.23
I-2	2.72	I-2	6.55
I-3	4.30	I-3	3.07
I-mix	2.95	I-mix	6.21
II-1	6.08	II-1	9.36
II-2	5.30	II-2	9.92
III-1	3.67	III-1	8.90
III-2	5.92	III-2	9.16
III-4	5.67	III-4	9.30

2.2 PAA polymer chain – DNQ-PAC interactions

The interactions between polymers and small molecules are difficult to be calculated by DFT methods due to the multiscale structures of the polymer and time-consuming calculations. MD simulations were therefore introduced to better understand the intrinsic behavior of the dry PSPI film formulations (**PF1** to **PF5**), and further to facilitate the optimal DNQ_PAC selection process by predicting the interactions between PAA polymer chains and DNQ_PAC molecules. The total energy (E_T), the kinetic energy (E_K) and the cohesive energy density (CED) and the density of the systems were computed (**Table 2**) for all the films.

Table 2 shows all computed *p*-PSPI films have negative ΔE_{mix} and χ_{AB} values, illustrating a good intermolecular miscibility and compatibility between DNQ PACs and the polymeric PAA component. This is consistent with the experimental observation that the mixtures of PAA and DNQ based photosensitizers are homogenous dark red resists. On the other hand, the converted IK compounds bring down the magnitude of both E_T and E_K in all film formulations, indicating their stability even upon UV irradiation. This is further supported by the decrease in the values of mixing energy and interaction parameter χ_{AB} , indicating a better intermolecular miscibility and compatibility between IK compounds and PAA polymer to form a more stable film network after UV exposure.

2.3 The dispersivity of DNQ PACs before and after UV exposure

It was reported that to increase the hydrophobicity, molecular size and dispersivity of DNQ PACs would improve the dissolution inhibition of a photoresist⁴. We therefore compared the dispersivity of DNQ PACs in the simulated films before and after UV exposure. The simulated morphologies of all unexposed film variants are shown in **Figure 3(a)**. When DNQ PACs converted to their indenylidene ketone (IK) analogues by UV light, the dipole moment of these IK compounds dramatically increased as shown in **Table 1**, resulting in a low hydrophobic property. **Figure 3(b)** illustrates that the *in silico* morphologies of all film variants showed the same trend to quite well mixed, evenly distributed polymer matrix except **PF1**, which composed with **I_{mix}** as PAC.

Table 2. Calculated density, CED and χ values of PAA-DNQ_PAC mixed systems considered in the present MD simulations

System	E_T (kcal/mol)	E_K (kcal/mol)	CED_{mix} (J/cm ³)	ΔE_{mix} (J/cm ³)	χ_{AB}
Before UV exposure					
PF1	182.4	1624.7	584	-19.2	-5.22
PF2	386.1	1663.1	581	-39.4	-10.7
PF3	686.2	1662.7	621	-43.0	-13.9
PF4	383.8	1664.5	682	-39.2	-13.8
PF5	396.7	1723.8	565	-17.3	-5.4
PF6	276.7	1666.9	576	-12.8	-4.6
PF7	281.9	1688.0	507	-13.6	-5.1
After UV exposure					
PF1	62.3	1549.5	584	-44.3	-5.6
PF2	191.1	1572.8	571	-28.1	-11.7
PF3	439.0	1570.2	660	-46.2	-13.9
PF4	288.6	1569.4	682	-50.7	-15.3
PF5	277.8	1633.4	578	-34.7	-9.9
PF6	15.1	1596.9	589	-42.4	-13.4
PF7	132.0	1619.9	562	-39.8	-12.2

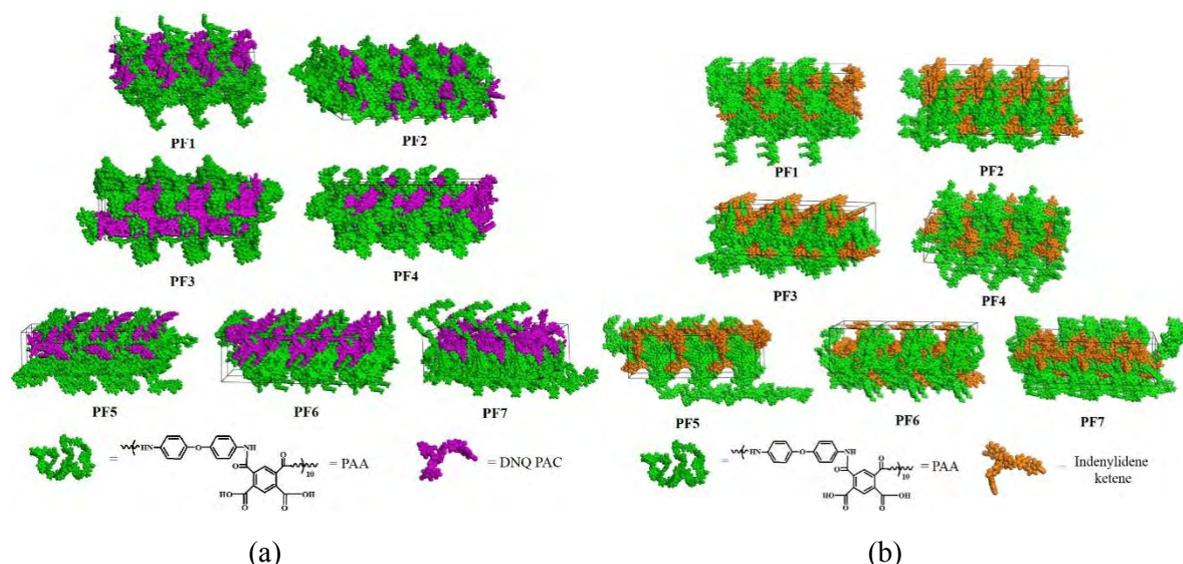


Figure 3. Distribution of DNQs in polymeric PAA matrix before (a) and after (b) UV exposure. Structures are represented by Corey-Pauling-Koltun (CPK) models, purple for DNQs, orange for indenyldene ketenes and green for PAA.

2.4 Possible dissolution mechanisms

With the skin layer protection mechanism as shown in **Figure 4**, the surface layer become more hydrophobic by covering with high concentration of PAC molecules and the solubility of this layer would be reduced. On the other hand, the surface would also become more compact due to the strong H-bonding interactions between PAC and PAA polymer. This would prevent or reduce the permeation

of the base developer and water through the surface layer, and subsequently reduce the dissolution rate of the unexposed area. After UV exposure, the PACs would distribute uniformly through the film based on computational observation, and promote the dissolution.

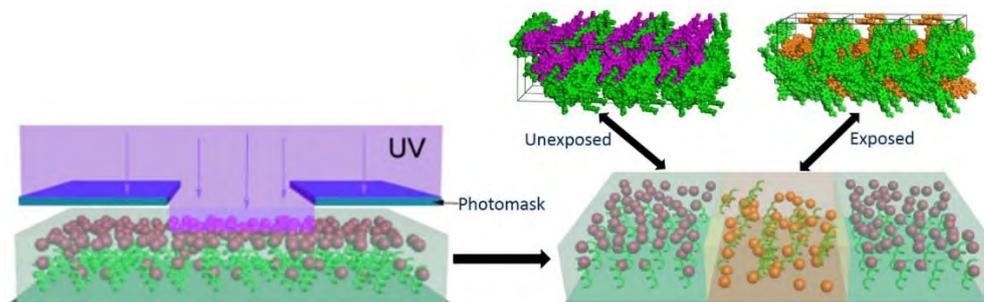


Figure 4. Schematic diagram of “skin layer” dissolution inhibition mechanism.

3. Conclusion

This study investigated the construction, screening, optimization, and evaluation of unexposed and exposed *p*-PSPI films containing PAA resist and various DNQ PACs employing atomistic molecular simulations. Among the PACs studied, the ones containing backbones with several mono-functional phenols, **III-1** to **III-3**, were calculated to have better dissolution inhibition by the formation of the “skin layer” with the gathering of PAC molecules on the film surface. The possible dissolution inhibition mechanisms for *p*-PSPIs should be the integration of the novolac-type H-bonding mechanism and the “skin layer” protectable mechanism, whereas the “skin layer” mechanism attributes a dominance protection against the film dissolution in developer. The “skin layer” is stabilized by the strong H-bonding interactions between PACs and PAA polymers to form a compact network. Overall, the capability of high performance atomistic molecular modeling approach to provide in-depth understanding of the possible dissolution inhibition effects of DNQ PACs onto *p*-PSPIs was well established.

4. References

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