chemistry proceedings

MDPI

Proceeding Paper

Unusual 1,1-Dicarboxylation Selectivity in the DominoHydrocarboxylation of Alkynes with Formate and Applicationin Polyimide Photoresists †

Yuting Zhu, Yaxin Sun and Peng Yang *

Shandong Provincial Key Laboratory of Photoresist, Key Laboratory of Molecular and Nano Probes, Ministry of Education, College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan 250014, China; email1@email.com (Y.Z.); email2@email.com (Y.S.)

* Correspondence: yangpeng@sdnu.edu.cn

† Presented at the 29th International Electronic Conference on Synthetic Organic Chemistry (ECSOC-29); Available online: https://sciforum.net/event/ecsoc-29.

Abstract

The fundamental principle of photolithography is that the crosslinking or degradation reaction of the photoresist causes a significant change in solubility. Traditional positive photoresists currently rely on the photoinduced decomposition of diazonaphthoquinone sulfonate (DNQ) or the deprotection of tert-butoxycarbonyl (Boc) groups to release carboxyl groups. However, there are several issues associated with these approaches: 1. DNQ is used in large quantities (25%) and is not heat-resistant; 2. Acid diffusion leads to increased line-edge roughness. To address these issues, we have developed a photoinduced alkyne domino 1,1-dicarboxylation reaction and applied this method to the working mechanism of positive photosensitive polyimide photoresists. This method can directly prepare water-soluble carboxyl-functionalized molecules and polymers from hydrophobic alkyne precursors. In this work, we synthesized five different types of photosensitive polyimides, all of which exhibited significant changes in solubility before and after exposure. Notably, this photochemical reaction is carried out under alkaline conditions, which can avoid acid corrosion that may affect the quality of the lithographic patterns. Moreover, under thermal treatment conditions, the residual alkyne groups can undergo crosslinking reactions, making the photoresist film more stable and providing better mechanical properties. This demonstrates the potential application value of our method in semiconductor manufacturing lithography technology.

Keywords: photosensitive polyimide; positive photoresist; acid diffusion

Academic Editor(s): Name

Published: date

Citation: Zhu, Y.; Sun, Y.; Yang, P. Unusual 1,1-Dicarboxylation Selectivity in the DominoHydrocarboxylation of Alkynes with Formate and Applicationin Polyimide Photoresists. *Chem. Proc.* **2025**, *volume number*, x. https://doi.org/10.3390/xxxxx

1. Introduction

Carboxylic acids and dicarboxylic acids are important chemicals and synthons with a wide range of applications in the pharmaceutical, agricultural, food, and polymer industries. The hydrocarboxylation of alkenes and alkynes is a straightforward route to synthesize high-value-added carboxylic acid derivatives (Figure 1a). Among them, visible-light-induced radical hydrocarboxylation [1–5] using inexpensive formate salts or carbon dioxide gas is becoming a greener alternative to the well-established transition-metal-catalyzed methods using carbon dioxide [6–8], carbon monoxide [9–11], or formic acid [12–14]. However, most of the established photoinduced radical hydrocarboxylation reactions

utilize active alkene substrates, while the relatively less reactive alkynes are rarely studied.The introduction should briefly place the study in a broad context and define the purpose of the work and its significance.

Additionally, the direct radical 1,1-dicarboxylation of alkynes has not yet been achieved. The significant difference in solubility between alkynes and carboxylic acids makes hydrocarboxylation and dicarboxylation photoreactions promising for application in positive-tone photolithography (Figure 1b). As designed, after a polymer containing alkynes is spin-coated onto a substrate (e.g., a silicon wafer), the coated film is exposed to ultraviolet light through a mask. The exposed areas will undergo carboxylation reactions and are washed away during the development process, thereby transferring the pattern information to the film. Unfortunately, there are currently no reports on the photoinduced carboxylation reactions of alkynes-containing polymers for positive-tone photolithography.

Herein, we report a novel finding on the divergent reaction outcomes of alkynes achieved via photoredox catalysis (Figure 1c). An aqueous solution of cesium formate (80% *w*/*w*) affords 1,1- or 1,2-dicarboxylic acid products with high selectivity, whereas cesium formate monohydrate (HCO2Cs·H2O) gives hydrocarboxylation products. This photoinduced reaction has been successfully employed to enhance the water solubility of five alkyne-containing polyimides and one alkyne-containing polystyrene, demonstrating its promising potential for application in photolithographic processing.

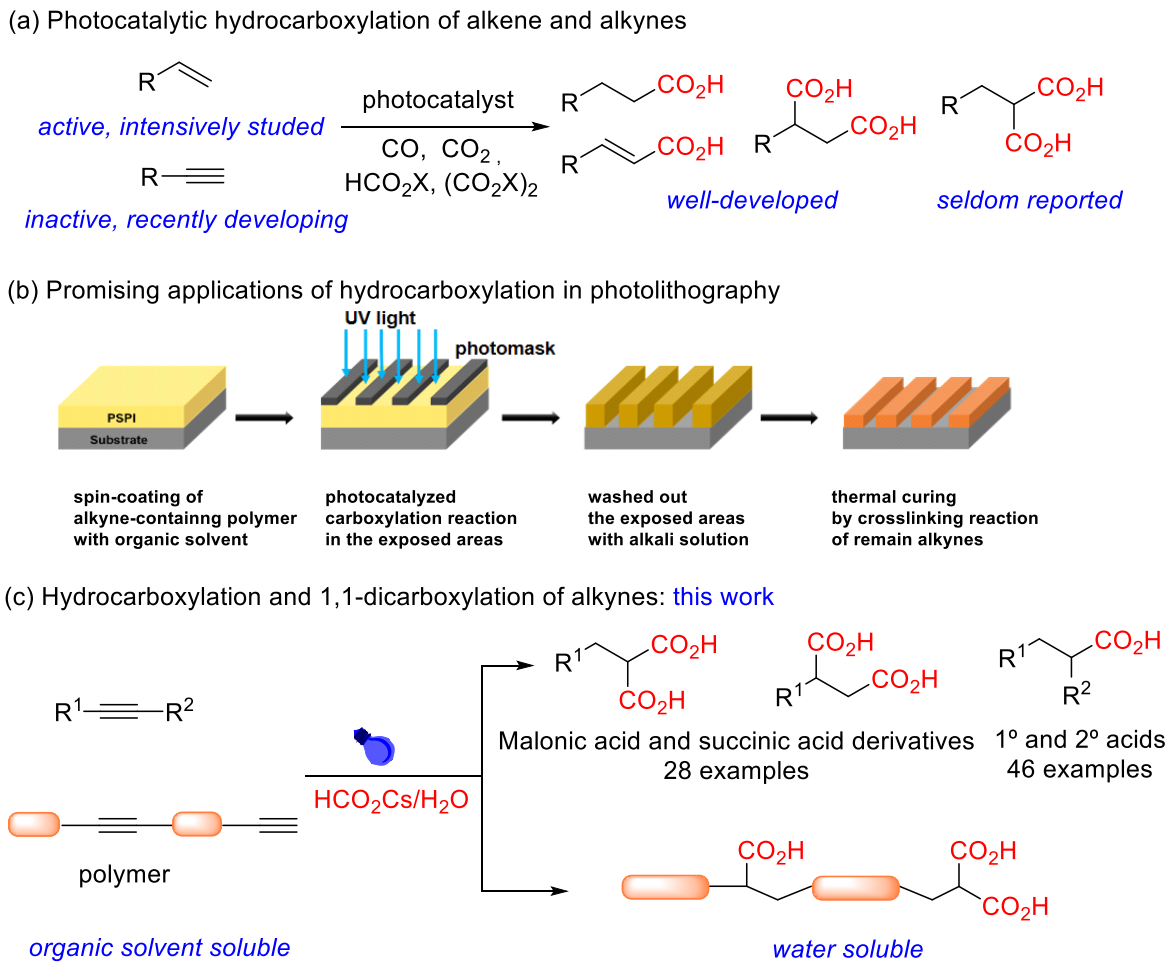
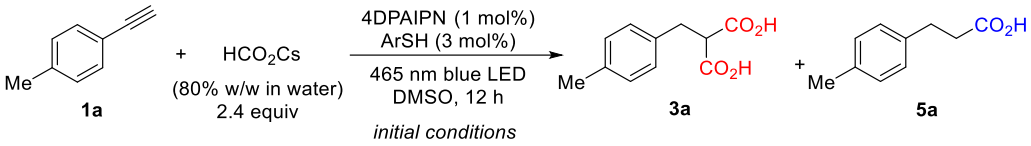


Figure 1. Development of hydrocarboxylation and dicarboxylation reactions, and potential application in positive-type photoresist.

2. Results and Discussion

We first explored a model photoreaction of 4-methyl-phenylacetylene 1a using 1% of 4DPAIPN as a photocatalyst,3% of methyl thiosalicylate as a hydrogen atom transfer catalyst (HAT), and 2.4 equivalents of HCO_2Cs (80% w/win water) as carbonyl source (Table 1). Irradiating by 30 W blue LED light (465 nm) in DMSO for 12 h, the reaction produced an aryl propionic acid 5a in 34% yield (Table 1, entry 1). We noticed that there was a small amount of precipitate in the reaction vial. After filtration and recrys-tallization, the white solid was determined by X-ray analysis to be a 1,1-dicaboxylated product 3a. Subsequently, we conducted a more in-depth exploration, optimized the conditions for the two products separately, and obtained the optimal yields for each.

Table 1. Condition optimizations.



Entry	Change from Initial Conditions	Yield of 3a	Yield of 5a
1	none	20	34
2	6.4 equiv HCO_2Cs (80% w/w in water)	71	24
3	8 equiv HCO_2Cs (80% w/w in water) (*Optional standard conditions A*)	82	13
4	3 equiv $HCO_2Cs.H_2O$, 7 equiv H_2O	24	64
5	3 equiv $HCO_2Cs.H_2O$, 10 equiv H_2O	14	30
6	3 equiv $HCO_2Cs.H_2O$, 7 equiv H_2O, and 10% ArSH (*Optional standard conditions B*)	12	82

The significant changes in solubility via cross-linking or degradation reaction of photoresist is the basic principle of the photolithography process. Most positive-type photoresists rely on the photo-induced decomposition of diazonaphtoquinone-sulfonic esters (DNQ) or deprotection of tert-butoxycarbonyl (Boc) group to release the carboxylic group which can be washed out by alkaline solutions so as to form pattern images. Their drawback is that the H+ generated in the exposed area will diffuse toward the unexposed area, thereby affecting the quality of the photolithography pattern. Our developed photoreaction occurred in basic conditions which can avoid acid corrosion. In addition, underheat treatment, residual alkynes can undergo cross-linking.

The two carboxylation products were characterized and confirmed by nuclear magnetic resonance (NMR) analysis:

The product of **3a**: ^{1}H NMR (400 MHz, MeOD) δ 7.11–7.05 (m, 4H), 3.59 (t, J = 7.8 Hz, 1H), 3.10 (d, J = 7.8 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, MeOD) δ 172.35, 136.98, 136.38, 129.84, 129.50, 54.97, 35.27, 20.85.

The product of **5a**: ^{1}H NMR (400 MHz, CDCl3) δ 11.32 (brs, 1H), 7.15 (s, 4H), 2.97 (t, J = 7.8 Hz, 2H), 2.71 (t, J = 7.8 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 179.75, 137.18, 135.97, 129.35, 128.25, 35.91, 30.25, 21.12.

To verify this hypothesis, we prepared five polyimides containing terminal and internal alkynes (for 365 nm photolithography) and one polystyrene (for 248 nm photolithography) (1q-1m, Figure 2a), and subjected them to the standard carboxylation conditions. After the photoreaction in DMSO, the mixture was diluted with ethyl acetate, and then the carboxylate salts of the polymers precipitated out, with the solid dissolving easily in water again (Figure 2b). To investigate whether the photoreaction can proceed under industrial light (i-line), we placed the reaction of polyimide 1ar on a plate with strip-

shaped grooves and successfully mimicked the photolithography process (Figure 2c). Under UV irradiation at 365 nm, the visible-light-driven tandem reaction proceeded smoothly, with the exposed areas being readily washed away by an alkaline solution while the unexposed areas remained undissolved. This may offer a new photoreaction for positive-type photoresists and a promising new working mode for photolithography technology.

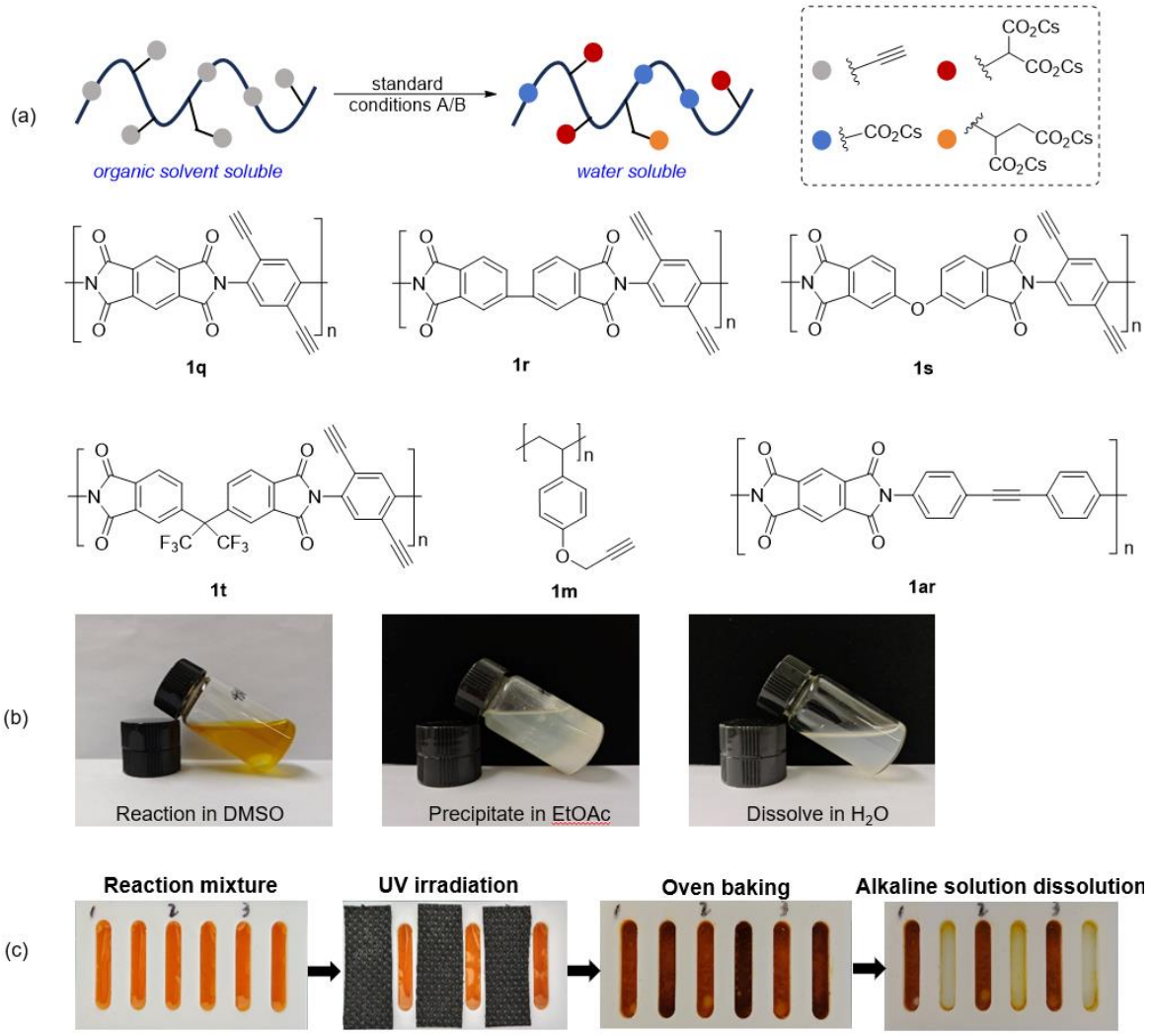


Figure 2. Post modification of photosensitive polyimide and mimic the photolithographic patterning processes.

3. Conclusions

In summary, we have discovered for the first time a novel photocatalyzed 1,1-dicarboxylation of alkynes. This photocatalyzed reaction has been creatively applied to the carboxylation of alkynes-containing polyimides and polystyrene, causing a significant change in their water solubility. It may provide a completely new working mode for positive-working photoresists for photolithographic processing.

Author Contributions:.

Funding: This research received no external funding.

Institutional Review Board Statement:

Informed Consent Statement:

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Song, L.; Wang, W.; Yue, J.-P.; Jiang, Y.-X.; Wei, M.-K.; Zhang, H.-P.; Yan, S.-S.; Liao, L.-L.; Yu, D.-G. *Nat. Catal.* **2022**, *5*, 832–838.
2. Zhang, W.; Chen, Z.; Jiang, Y.-X.; Liao, L.-L.; Wang, W.; Ye, J.-H.; Yu, D.-G. *Nat. Commun.* **2023**, *14*, 3529.
3. Huang, H.; Ye, J.-H.; Zhu, L.; Ran, C.-K.; Miao, M.; Wang, W.; Chen, H.; Zhou, W.-J.; Lan, Y.; Yu, B.; et al. CCS Chem 2021, 3,1746–1756.
4. Alektiar, S.N.; Wickens, Z.K. *J. Am. Chem. Soc.* **2021**, *143*, 13022–13028.
5. Alektiar, S.N.; Han, J.; Dang, Y.; Rubel, C.Z.; Wickens, Z.K. *J. Am. Chem. Soc.* **2023**, *145*, 10991–10997.
6. Gaydou, M.; Moragas, T.; Juliá-Hernández, F.; Martin, R. *J. Am. Chem. Soc.* **2017**, *139*, 12161–12164.
7. Meng, Q.-Y.; Wang, S.; Huff, G.S.; König, B. *J. Am. Chem. Soc.***2018**, *140*, 3198–3201.
8. Xiong, W.; Shi, F.; Cheng, R.; Zhu, B.; Wang, L.; Chen, P.; Lou, H.; Wu, W.; Qi, C.; Lei, M.; et al. *ACS Catal.* **2020**, *10*, 7968–7978.
9. Konrad, T.M.; Fuentes, J.A.; Slawin, A.M.Z.; Clarke, M.L. *Angew. Chem. Int. Ed.* **2010**, *122*, 9197–9200; *Angew. Chem.* **2010**, *122*, 9383–9386.
10. Sang, R.; Kucmierczyk, P.; Dühren, R.; Razzaq, R.; Dong, K.; Liu, J.; Jackstell, R.; Beller, M. *Angew. Chem. Int. Ed.* **2019**, *131*, 14365–14373; *Angew. Chem.* **2019**, *131*, 14503–14511.
11. Li, J.; Shi, Y. *Chem. Soc. Rev.* **2022**, *51*, 6757–6773.
12. Yang, P.; Sun, Y.; Fu, K.; Zhang, L.; Yang, G.; Yue, J.; Ma, Y.; Zhou, J.S.; Tang, B. *Angew. Chem. Int. Ed.* **2022**, *61*, e202111778; *Angew. Chem.* **2022**, *134*, e202111778.
13. Xia, S.-M.; Yang, Z.-W.; Chen, K.-H.; Wang, N.; He, L.-N. *Chin. J. Catal.* **2022**, *43*, 1642–1651.
14. Ren, W.; Sheng, X.; Shi, Y. *Org. Lett.* **2024**, *26*, 6174–6178.