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Article

Photo-Iniferter RAFT Synthesis of Versatile, Nonalternating Poly(acrylate-*co*-isocyanides)

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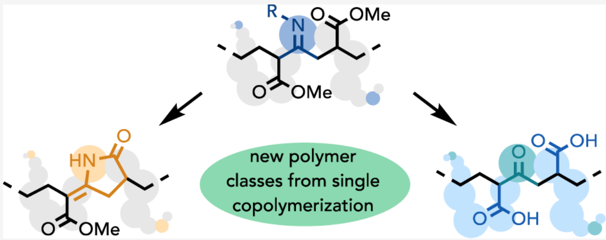
ABSTRACT: Nonalternating poly(isocyanide-*co*-acrylate) copolymers enable access to novel polymer microstructures with versatile chemistry and allow for designed mechanical properties, an important facet of combating the plastic waste crisis. While previous syntheses used cobalt-mediated radical polymerizations, the cobalt complex exhibits side reactivity, complicating control over polymerization. This work describes the application of an orthogonal, photocontrolled RAFT polymerization to a range of isocyanides with excellent temporal control. Under solvent-free conditions, adding monomers with a standard chain transfer agent (CTA) results in the synthesis of copolymers that are then transformed into several novel microstructures. Interestingly, we discover that the isocyanide units can undergo cyclization of the backbone, resulting in an unexampled polyamide-like copolymer containing the pyrrolidone ring. Moreover, we generate poly(acrylic acid)-like copolymers with small amounts of ketone linkages through hydrolysis, enabling faster degradation rates for this class of polymer.



INTRODUCTION

In recent years, our reliance on plastics has reached unprecedented levels, fundamentally altering nearly every aspect of modern life. While the versatility, durability, and affordability of plastics have made them indispensable, their widespread use has inadvertently led to a global crisis. The rampant production and improper disposal of single-use plastics and their persistent presence in the environment have underscored the urgent need for innovative solutions.[1−4] To combat this looming crisis, a paradigm shift toward developing and adopting new materials is imperative. These materials must not only replicate the functionalities of existing plastics but also prioritize sustainability, degradability, and reduced environmental impact.[5−13] Carbonyl-containing polymers are of great interest due to their susceptibility to photodegradative pathways under ultraviolet (UV) light irradiation, such as Norrish cleavages.[14−17] Introducing minimal carbonyl content facilitates breakdown in the environment and maintains parent physical properties; however, realizing such commercial materials has proven difficult.[18−31]

Recently, our group employed a novel cobalt-mediated radical polymerization (CMRP) using a cobalt-hydride (Co−H) initiating species to copolymerize acrylate monomers with isocyanides to generate nonalternating poly(isocyanides-*co*-acrylates) (Scheme 1).[32−43] Implementing a reversible deactivation radical polymerization (RDRP) attenuated unproductive termination and chain transfer events and provided control over polymer molecular weights and dispersity.[44−47] Incorporating an isocyanide resulted in an imine linkage in the backbone of the polymer, creating an avenue to various microstructures, including facile tautomerization to the enamine. Importantly, this approach allowed the production of nonalternating polyketones via hydrolysis of the imine. Ultimately, we demonstrated the manipulation of thermal properties and degradation rates by controlling the degree of incorporation and the microstructure.[48]

This new material class alludes to interesting chemistry and adaptability—the responsive characteristics imparted by the imine can be selectively modified at different points in the polymers' lifetime to be upcycled into new materials with tunable characteristics. Alas, the use of isocyanides in radical polymerizations is sparsely reported.[49−53] Expanding the isocyanide scope is necessary to apply this approach more universally to existing commodity polymers. Despite the control afforded by the Co−H initiated CMRP protocol, deactivation of the cobalt complex by ligation of the isocyanide and poor chain end fidelity limited the synthesis of more advanced polymer microstructures.

To expand the scope and applicability of the copolymerization of isocyanides, we sought to use photoiniferter reversible addition−fragmentation chain transfer (PI-RAFT) (Scheme 1).[54−56] Using light for initiation offers spatiotemporal regulation over the polymerization without exogenous photo-

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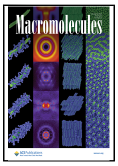

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Scheme 1. Previous Work Set the Precedent of Radical Copolymerization of Isocyanides with Various Acrylates, Followed by this Work Using a Photocontrolled Approach with Various Isocyanides, Accessing More Divergent Copolymers

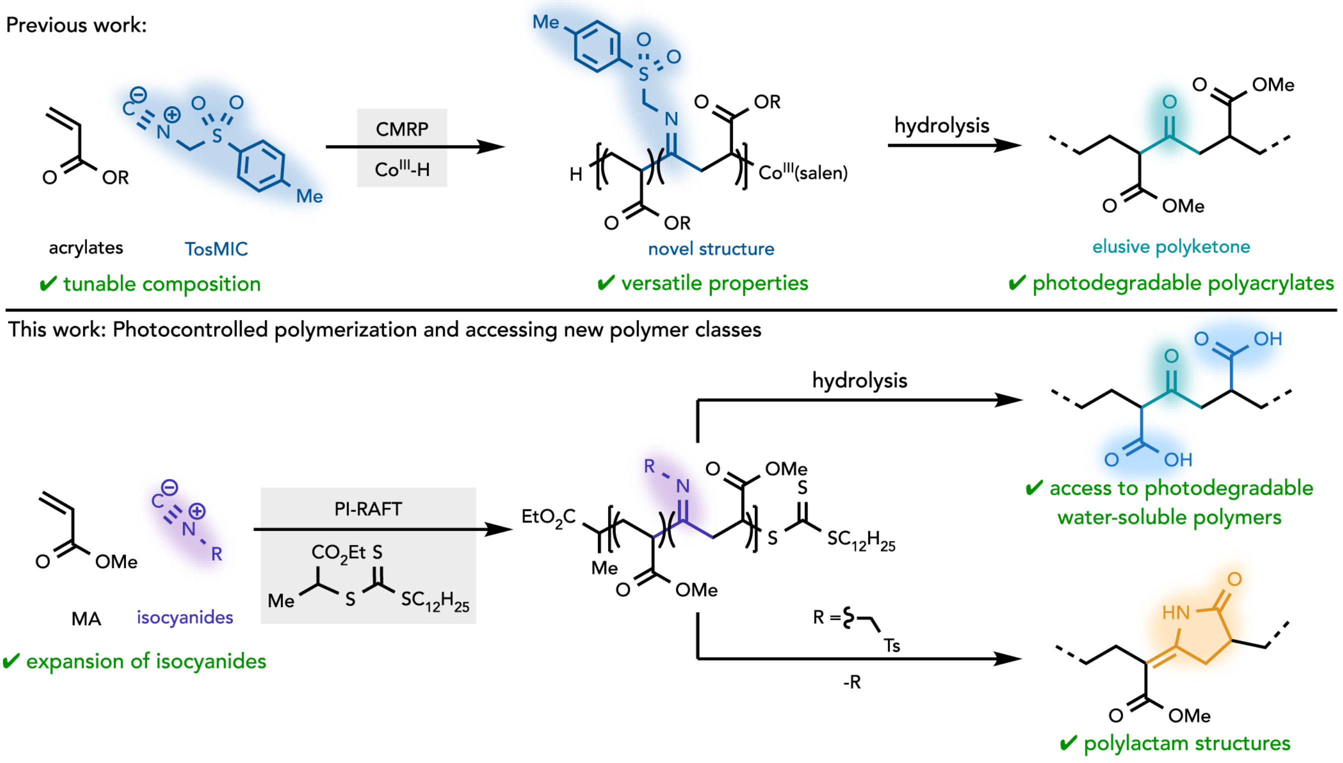
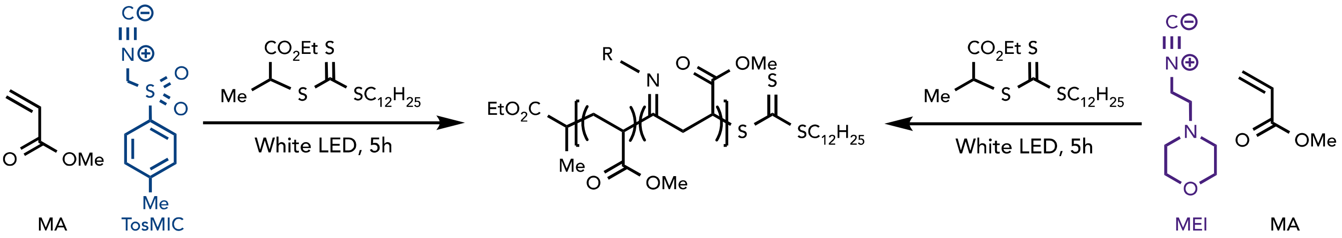


Table 1. Initial PI-RAFT Polymerizations of Methyl Acrylate and TosMIC or MEI[a]



Entry	DP	MA:TosMIC	M_n^{crude}	$Đ$	$Inc^{\cdot exp}$	$Inc^{\cdot theo}$	Entry	DP	MA: MEI	M_n^{crude}	$Đ$	$Inc^{\cdot exp}$	$Inc^{\cdot theo}$
1	200	90:10	11.6	1.08	2.4%	3.3%	6	200	90:10	8.0	1.16	3.4%	3.5%
2	400	90:10	16.0	1.19	3.0%	3.7%	7	400	90:10	21.1	1.14	3.4%	3.8%
3	600	90:10	22.1	1.19	3.1%	3.6%	8	600	90:10	28.4	1.23	3.6%	4.0%
4	200	95:5	9.6	1.04	1.4%	1.9%	9	200	95:5	12.9	1.09	2.2%	3.3%
5	200	85:15	10.1	1.18	3.8%	3.8%	10	200	85:15	12.4	1.19	4.9%	4.9%

[a] DP = [Total Monomer]/[CTA]. $Inc^{\cdot exp}$ represents mol % incorporation of the isocyanide. Theoretical incorporation ($Inc^{\cdot theo}$) is calculated based on monomer conversion (see Supporting Information for more details). Molecular weight values are in kg/mol.

catalysts. Previous attempts to use light mediation on our CMRP protocol were unsuccessful. Additionally, this offers a simpler 3-component system (the two comonomers and CTA) and no monomer addition sequence limitation as was seen in the Co−H initiated CMRP system that required addition of the isocyanide immediately after hydrometalation. Additionally, use of PI-RAFT avoids the use of transition metals, affording a metal-free polymerization strategy and circumventing any coordination of the polymer to the metal complex at higher conversions. In this work, PI-RAFT polymerization was employed via direct activation of the chain transfer agent (CTA) by light to obtain copolymers from methyl acrylate (MA) and a broadened isocyanide scope while providing superb chain end control. Here, we demonstrate the successful employment of a scope of isocyanides and aim to show the utility of the generated copolymers in accessing unprecedented microstructures, like polylactams and photodegradable water-soluble materials.[57]

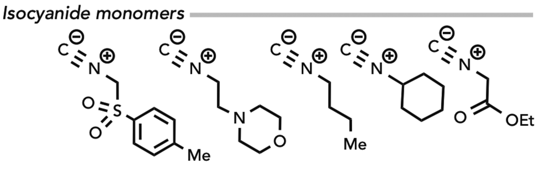
■ RESULTS AND DISCUSSION

To begin the implementation of a PI-RAFT protocol, *S*-1-dodecyl-*S*'-((2-ethoxycarbonyl)eth-2-yl) trithiocarbonate was selected as the CTA for its previous use in acrylate polymerization. Upon broad-spectrum light irradiation, using a 90:10 feed ratio of MA to *p*-toluenesulfonylmethyl isocyanide (TosMIC), a copolymer consisting of 2.4 mol % isocyanide incorporation was achieved while maintaining low dispersity and close agreement between experimental and theoretical molecular weight, indicative of a controlled polymerization (Table 1, Entry 1). Increasing the ratio of monomers to CTA achieved larger molecular weight polymers with low dispersity (Table 1, Entries 2 and 3). By altering the feed ratio of each comonomer, we obtained targeted copolymer compositions that ranged from 1.4 to 3.8 mol % isocyanide (Table 1, Entries 4 and 5). This demonstrates that the initial monomer feed ratio can be used to tune the copolymer composition.

We then explored using 2-morpholinoethyl isocyanide (MEI) as an electronically and sterically alternative isocyanide. With the established protocol, MEI was successfully copolymerized with MA. Using the same starting monomer ratios of 90:10, we see higher incorporation (3.4 mol %) relative to TosMIC, with a similar degree of control over molecular weights and dispersity (Table 1, Entry 6). Likewise, higher degrees of polymerization (DPs) yield larger polymers, and incorporation remains consistent (Table 1, Entries 7 and 8). Altering the initial feed ratios gave polymers with 2.2 to 4.9 mol % incorporation (Table 1, Entries 9 and 10). Overall, the agreement between experimental and theoretical incorporation is better using MEI (Table 1). In RAFT polymerizations, the identity of the CTA is very important for compatibility of different monomer classes. Because isocyanides have not been utilized in RAFT polymerizations before, we wanted to explore the effect that changing the substituents on a CTA would have on either the degree of incorporation or control over the polymerization. The identity of the CTA was changed and the effect on the copolymerization was studied (Table S4). Dithiocarbamates and xanthates were successful, however loss of control was observed. Meanwhile, dithiobenzoates were unsuccessful in polymerization.[58] Notably, while loss of control occurred when the xanthate was employed, we did observe slightly higher incorporation and better agreement between experimental and theoretical incorporation, suggesting an exciting area to optimize for isocyanide copolymerizations in the future.

We explored various isocyanides to expand the comonomer scope and compare the effect of different electronic and structural properties (Table 2). In addition to TosMIC and MEI, *n*-butyl isocyanide (BI), cyclohexyl isocyanide (CI), and ethyl isocyanoacetate (EI), were copolymerized with good control. In contrast, several aromatic isocyanides were unsuccessful, not reaching sufficient conversion in the same time frame (Table S5). Electron-donating substituents lead to an increase in incorporation, while the steric bulk seems to be a hindrance to efficient polymerization.

Table 2. Scope of Isocyanides Successfully copolymerized with MA



	TosMIC	MEI	BI	CI	EI
MA / Icyn Conv. (%)	52 / 16	57 / 18	41 / 9	38 / 10	43 / 9
M_n (kg/mol)	11.6	8.0	11.0	9.0	10.2
Đ	1.08	1.16	1.04	1.05	1.23
Incorp. (%)	2.4	3.3	3.3	1.7	3.0

Kinetic analysis of the monomer conversions of the MA-TosMIC copolymerization initially showed linear first-order kinetics (Table S6). At higher conversions, there was an increase in deviation from linearity. However, the isocyanide did not shut down the polymerization. By comparison, the deviation from linearity is smaller when using MEI, and the conversion is more competent. Overall, we saw a linear molecular weight increase with conversion, which agreed with the theoretical molecular weight, and low dispersity throughout the polymerization (Figure 1a).

The CTA chain end could be identified by NMR in the purified polymer sample, leading us to further examine and exploit the chain end fidelity of the copolymers. This enabled us to form block copolymers by chain extension. The poly(MA-*co*-MEI) copolymer was synthesized and purified by precipitation. The polymer was then redissolved and irradiated with *n*-butyl acrylate (*n*BA), forming a diblock copolymer. The polymer molecular weight increased from 12.4 to 58.6 kg/mol with low dispersities of 1.06 and 1.04, respectively. These values are in good agreement with theoretical molecular weights. The unimodal shift in the GPC trace suggests efficient reinitiation and controlled chain extension with good chain end fidelity, which we calculated to be 84% from the residual unreacted chains (Figure 1b). The copolymer synthesized from MEI exhibited slightly better chain end fidelity than those synthesized using TosMIC (Figures S3 and S4).

We performed the polymerization with intermittent light irradiation to highlight the potential for temporal control afforded by using light as a stimulus. Gratifyingly, the polymerization showed no conversion without light (Figure 1c). Monomer conversion and molecular weight growth were only seen when the light was turned on, and dispersities remained low throughout.

The conformation of the copolymers obtained via the PI-RAFT protocol was examined to ensure the incorporation of the isocyanide in the backbone. For the poly(MA-*co*-MEI) copolymers, we observed peaks in the ^{1}H NMR around 3.7, 3.5, 2.7, and 2.5 ppm, indicating MEI incorporation as well as proton signals at 9.4 and 9.2 ppm, indicating tautomerization to the β-enamine ester, as seen with poly(MA-*co*-TosMIC). The BI and EI copolymers also exhibit two protons near 9.4 ppm indicating tautomerization to the enamine. Through ^{1}H−^{15}N heteronuclear single quantum coherence (HSQC) and ^{1}H−^{13}C heteronuclear multiple bond coherence (HMBC) nuclear magnetic resonance (NMR) experiments, these protons and their correlated nitrogens and carbons have similar chemical shifts, indicating *E*/*Z* isomers of the C−N bond of the enamine (see Supporting Information for details). Typically, the *E* conformation is the major isomer present due to the proximity of the ester carbonyl, which is capable of hydrogen bonding to the enamine proton. However, we believe there is a higher percentage of *Z* conformers due to steric restrictions within the polymer. Interestingly, the CI copolymer shows only one isomer under similar conditions (see Supporting Information for details). We hypothesize that this is due to the increased steric restriction from the cyclohexyl group on the nitrogen.

The conformation of the poly(MA-*co*-TosMIC) copolymers was more interesting. We observed tautomerization to the enamine and the appearance of an enamine proton downfield

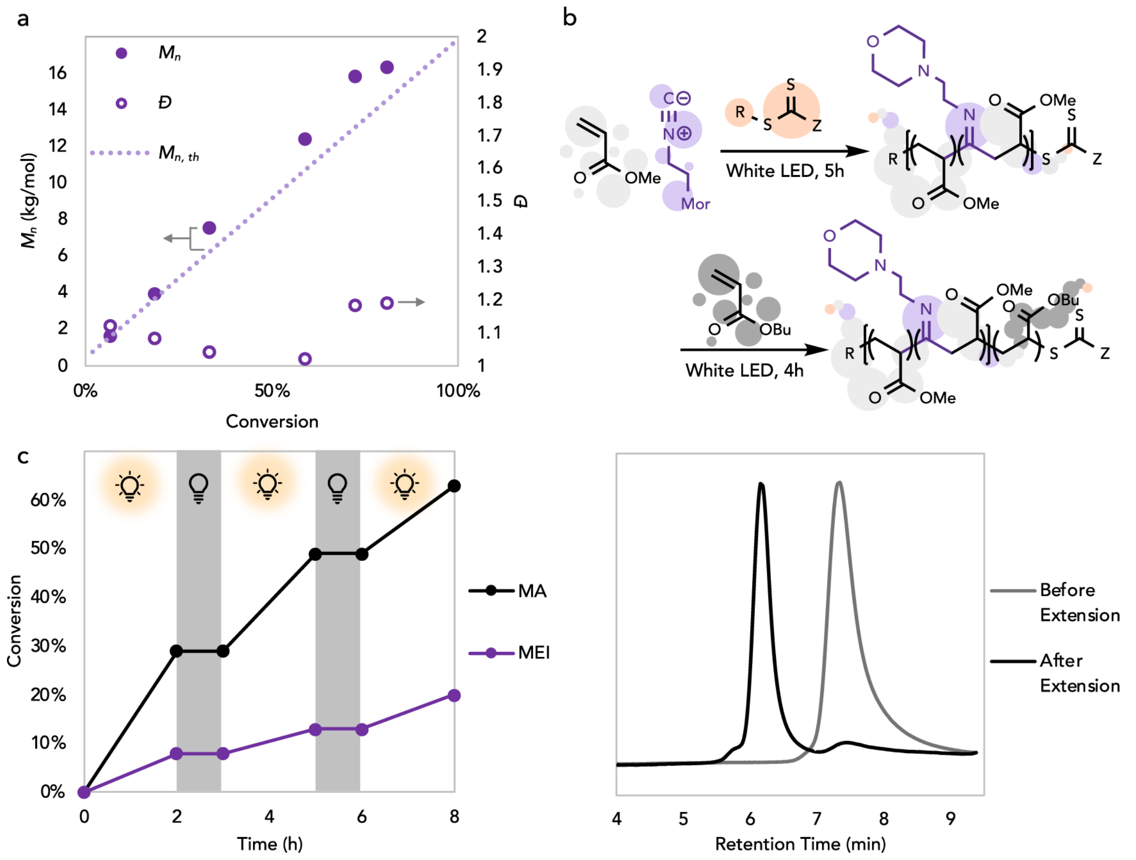


Figure 1. a) Molecular weight plotted against the averaged conversion of MA and MEI via PI-RAFT. b) Chain extension of poly(MA-*co*-MEI) copolymers with *n*BA. c) Plot of monomer conversion over time as the light is turned on and off periodically throughout the polymerization.

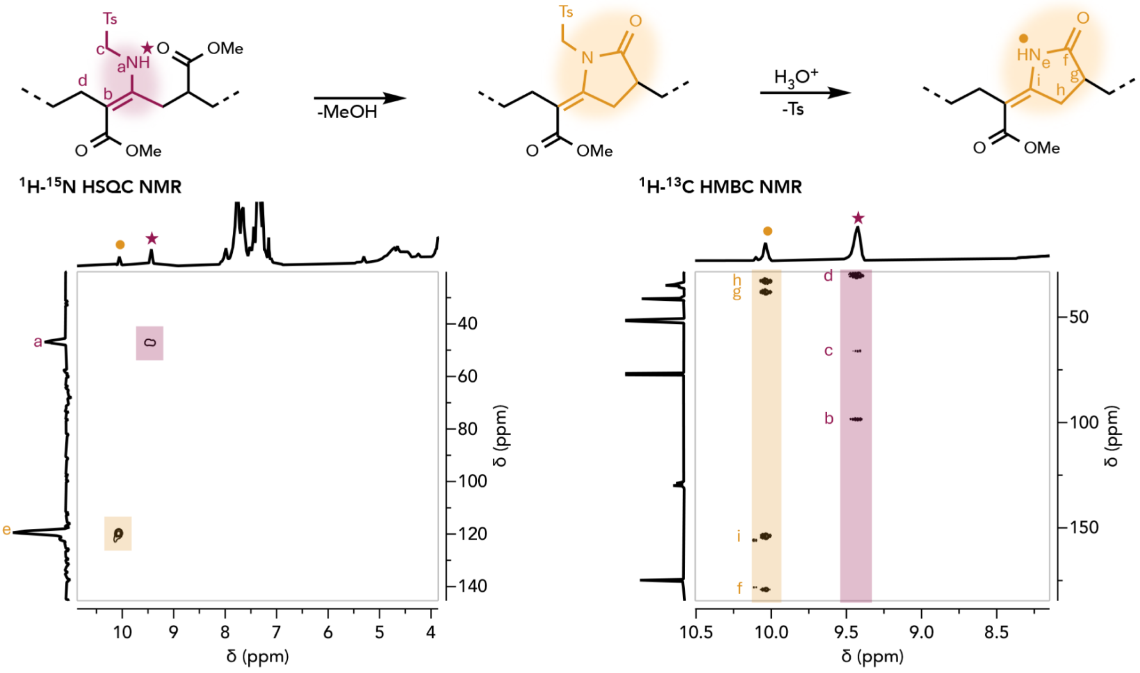


Figure 2. Evidence of lactamization of poly(MA-*co*-TosMIC) through ^{1}H−^{15}N HSQC and ^{1}H−^{13}C HMBC NMR experiments.

at 9.4 ppm, which correlates to a nitrogen with a chemical shift (47 ppm) similar to that of amines from ^{1}H−^{15}N HSQC NMR experiments (Figure 2).[59] Excitingly, we see the appearance of a proton signal slightly downfield at 10 ppm that, from ^{1}H−^{15}N HSQC and ^{1}H−^{13}C HMBC NMR experiments, correlates to nitrogens and carbons of significantly different chemical shifts, signifying a drastic change in the structure, exclusive to the TosMIC copolymer. We assigned these signals as an amide structure supporting lactamization of the backbone from the favorable release of sulfinic acid and subsequent hydrolysis (Figure 2). We observe this to occur slowly over time in solution, presumably in the presence of adventitious water. Upon heating, almost quantitative conversion of the enamine to the lactam can be seen (Figure S25). Meanwhile, the MEI-containing copolymer does not show any change in NMR or FT-IR characterization under similar conditions, supporting no lactamization of that structure. Ultimately, this is an exciting phenomenon and a very useful tool for generating lactam rings in the polymer backbone, another new microstructure. A few reports have used condensation polymerization to generate polyamides with nitrogen linkages in the backbone; however, 1,3 linkages have not been reported.[60−63] Significantly, pyrrolidone-containing polylactams are predicted to have high glass transition temperatures due to the rigidity imparted from the heterocycles and have higher rates of biodegradation. These have rarely been studied due to the lack of synthetic methods to generate these materials. Upon DSC analysis, the lactam-containing copolymer has a lower glass transition temperature (T_g) than the original TosMIC-containing copolymer but higher than the MEI-containing copolymer (Figures S8, S12, S24, and S30). Additional studies will need to be performed to see if these lactam rings can be leveraged to affect the thermomechanical properties of these novel materials.

Because accessing multiple microstructures from a single copolymerization is an attractive quality for a versatile material, we sought to demonstrate sequential hydrolysis of the functional groups. Using mild conditions previously reported, poly(MA-*co*-MEI) was successfully hydrolyzed to poly(MA-*co*-ketone), identical to that synthesized from the hydrolysis of poly(MA-*co*-TosMIC), confirmed by NMR analysis (Figure 3). We then sought to fully hydrolyze these copolymers to poly(acrylic acid)-like polymers under more forcing conditions. Polyacrylic acids (PAAs) and sodium polyacrylate-based materials are synthetic polymers known for their water-absorbing and adhesive properties,[64−66] with an estimated annual production of around 2 million metric tons.[67] However, PAA is challenging to recycle or degrade due to the difficulty of removal from the environment and its stable molecular structure.[68−71] Through our conditions, these polyacrylic acid-like materials will have embedded photodegradable carbonyl linkages, offering a degradable pathway for this class of polymers.[72] Using conditions previously reported by the Sumerlin group,[73] the rate of hydrolysis of the homopolymers was first studied. Homopolymers of *t*-butyl acrylate hydrolyzed quickest, followed by MA and phenyl acrylate (Table S11). Gratifyingly, the poly(MA-*co*-ketone) was hydrolyzed further, and the resultant structures were confirmed through NMR experiments. The appearance and then shift of the ^{13}C signal from the ketone carbonyl revealed nonalternating poly(acrylic acid-*co*-ketones) (see Supporting Information for details). This privileged structure has not been reported through direct or indirect synthetic methods. Additionally, the direct transformation of the poly(MA-*co*-isocyanide) copolymers to poly(acrylic acid-*co*-ketones) could be realized using the second set of conditions.

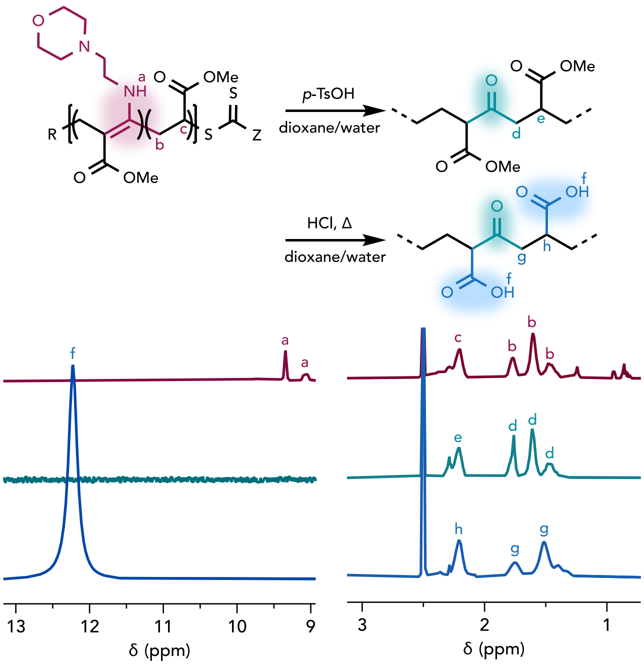


Figure 3. Sequential hydrolysis of multiple microstructures. Overlaid spectra from 9 to 13 ppm are on different scales to clearly distinguish peaks at different chemical shifts.

Lastly, the introduction of ketones to polyacrylic acid enabled photodegradation. Upon irradiation with 390 nm light, the degradation of the nonalternating poly(acrylic acid-*co*-ketones) was examined. We found a modest molecular weight decrease consistent with our previous studies, supporting that minimal carbonyl content is sufficient for chain scission and enhanced degradation rates of these copolymers compared to the parent polymer (Table S10). Because these water-soluble polymers cannot be reclaimed from the environment, installing this photodegradable linkage is a potential means of breaking down these materials.

■ CONCLUSIONS

This article shows that new microstructures with entirely different characteristics can be generated from a single copolymerization protocol. We can access unprecedented polylactams, as well as polyacrylic acids, with enhanced rates of photodegradation. This approach offers the synthesis of novel copolymers, showing promise to replace single-use plastics as one that can be continually repurposed or broken down in the environment, providing the pathway for a nonaccumulative waste stream.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.4c01610.

Details of experimental procedures and additional supplementary results (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Chamas, A.; Moon, H.; Zheng, J.; Qiu, Y.; Tabassum, T.; Jang, J. H.; Abu-Omar, M.; Scott, S. L.; Suh, S. Degradation Rates of Plastics in the Environment. *ACS Sustainable Chem. Eng.* **2020**, *8* (9), 3494−3511.

(2) Min, K.; Cuiffi, J. D.; Mathers, R. T. Ranking Environmental Degradation Trends of Plastic Marine Debris Based on Physical Properties and Molecular Structure. *Nat. Commun.* **2020**, *11* (1), 727.

(3) Ellen MacArthur Foundation. *The New Plastics Economy: rethinking The Future Of Plastics And Catalysing Action*. Ellen MacArthur Foundation, 2017. https://www.ellenmacarthurfoundation.org/publications/the-new-plastics-economy-rethinking-the-future-of-plastics-catalysing-action. accessed July 23 2022.

(4) Hoornweg, D.; Bhada-Tata, P.; Kennedy, C. Environment: Waste production must peak this century. *Nature* **2013**, *502*, 615−617.

(5) García, J. M. Catalyst: Design Challenges for the Future of Plastics Recycling. *Chem* **2016**, *1* (6), 813−815.

(6) Zhu, Y.; Romain, C.; Williams, C. K. Sustainable Polymers from Renewable Resources. *Nature* **2016**, *540* (7633), 354−362.

(7) Abel, B. A.; Snyder, R. L.; Coates, G. W. Chemically Recyclable Thermoplastics from Reversible- Deactivation Polymerization of Cyclic Acetals. *Science* **2021**, *373* (6556), 783−789.

(8) Shieh, P.; Zhang, W.; Husted, K. E. L.; Kristufek, S. L.; Xiong, B.; Lundberg, D. J.; Lem, J.; Veysset, D.; Sun, Y.; Nelson, K. A.; Plata, D. L.; Johnson, J. A. Cleavable Comonomers Enable Degradable, Recyclable Thermoset Plastics. *Nature* **2020**, *583* (7817), 542−547.

(9) Fagnani, D. E.; Tami, J. L.; Copley, G.; Clemons, M. N.; Getzler, Y. D. Y. L.; McNeil, A. J. 100th Anniversary of Macromolecular Science Viewpoint: Redefining Sustainable Polymers. *ACS Macro Lett.* **2021**, *10* (1), 41−53.

(10) Li, Z.; Zhang, X.; Zhao, Y.; Tang, S. Mechanochemical Backbone Editing for Controlled Degradation of Vinyl Polymers. *Angew. Chem., Int. Ed.* **2024**, *63*, 33.

(11) Rapagnani, R. M.; Dunscomb, R. J.; Fresh, A. A.; Tonks, I. A. Tunable and recyclable polyesters from CO_2 and butadiene. *Nat. Chem.* **2022**, *14*, 877−883.

(12) Tang, S.; Lin, B.-L.; Tonks, I. A.; Eagan, J. A.; Ni, X.; Nozaki, K. Sustainable Copolymer Synthesis from Carbon Dioxide and Butadiene. *Chem. Rev.* **2024**, *124* (6), 3590−3607.

(13) Yee, G. M.; Wang, T.; Hillmyer, M. A.; Tonks, I. A. Mechanistic Study of Palladium-Catalyzed Hydroesterificative Copolymerization of Vinyl Benzyl Alcohol and CO. *Organometallics* **2019**, *38* (8), 1778−1786.

(14) Brubaker, M. M.; Coffman, D. D.; Hoehn, H. H. Synthesis and Characterization of Ethylene/Carbon Monoxide Copolymers, A New Class of Polyketones 1. *J. Am. Chem. Soc.* **1952**, *74* (6), 1509−1515.

(15) Hartley, G. H.; Guillet, J. E. Photochemistry of Ketone Polymers. I. Studies of Ethylene-Carbon Monoxide Copolymers. *Macromolecules* **1968**, *1* (2), 165−170.

(16) Nozaki, K.; Ito, S. *Polymer Science: a Comprehensive Reference* **2012**, 825−842.

(17) Morgen, T. O.; Baur, M.; Göttker-Schnetmann, I.; Mecking, S. Photodegradable Branched Polyethylenes from Carbon Monoxide Copolymerization under Benign Conditions. *Nat. Commun.* **2020**, *11* (1), 3693.

(18) Coffman, D. D.; Pinkney, P. S.; Wall, F. T.; Wood, W. H.; Young, H. S. Compositional Relationships in the Copolymerization of Ethylene with Carbon Monoxide. *J. Am. Chem. Soc.* **1952**, *74* (13), 3391−3393.

(19) Drent, E.; Dijk, R. V.; Ginkel, R. V.; Oort, B. V.; Pugh, R. I. The First Example of Palladium Catalysed Non-Perfectly Alternating Copolymerisation of Ethene and Carbon Monoxide. *Chem. Commun.* **2002**, No. 9, 964−965.

(20) Nakamura, A.; Munakata, K.; Kochi, T.; Nozaki, K. Regiocontrolled Copolymerization of Methyl Acrylate with Carbon Monoxide. *J. Am. Chem. Soc.* **2008**, *130* (26), 8128−8129.

(21) Nakamura, A.; Munakata, K.; Ito, S.; Kochi, T.; Chung, L. W.; Morokuma, K.; Nozaki, K. Pd-Catalyzed Copolymerization of Methyl Acrylate with Carbon Monoxide: Structures, Properties and Mechanistic Aspects toward Ligand Design. *J. Am. Chem. Soc.* **2011**, *133* (17), 6761−6779.

(22) Čamdžić, L.; Haynes, C. A.; Stache, E. E. An old polymer class revisited: Versatile, degradable, non-alternating polyketones. *Chem* **2024**, *10*, 1357.

(23) Carrow, B. P.; Nozaki, K. Transition-Metal-Catalyzed Functional Polyolefin Synthesis: Effecting Control through Chelating Ancillary Ligand Design and Mechanistic Insights. *Macromolecules* **2014**, *47* (8), 2541−2555.

(24) Tang, S.; Seidel, F. W.; Nozaki, K. High Density Polyethylenes Bearing Isolated In-Chain Carbonyls. *Angew. Chem., Int. Ed.* **2021**, *60* (51), 26506−26510.

(25) Baur, M.; Lin, F.; Morgen, T. O.; Odenwald, L.; Mecking, S. Polyethylene Materials with In-Chain Ketones from Nonalternating Catalytic Copolymerization. *Science* **2021**, *374* (6567), 604−607.

(26) Chen, S.-Y.; Pan, R.-C.; Chen, M.; Liu, Y.; Chen, C.; Lu, X.-B. Synthesis of Nonalternating Polyketones Using Cationic Diphosphazane Monoxide-Palladium Complexes. *J. Am. Chem. Soc.* **2021**, *143* (28), 10743−10750.

(27) Sen, A. Chromatography/Foams/Copolymers. *Adv. Polym. Sci.* **2005**, 125−144.

(28) Chatgilialoglu, C.; Crich, D.; Komatsu, M.; Ryu, I. Chemistry of Acyl Radicals. *Chem. Rev.* **1999**, *99* (8), 1991−2070.

(29) Arrington, K. J.; Murray, C. B.; Smith, E. C.; Marand, H.; Matson, J. B. Precision Polyketones by Ring-Opening Metathesis Polymerization: Effects of Regular and Irregular Ketone Spacing. *Macromolecules* **2016**, *49* (10), 3655−3662.

(30) Fuchs, A.; Mecking, S. Controlled Cobalt-Mediated Free-Radical Co- and Terpolymerization of Carbon Monoxide. *J. Am. Chem. Soc.* **2022**, *144*, 15879.

(31) Lo, S.-Y.; Folster, C. P.; Harkins, R. P.; Anderson, R. J.; Lien, Y.-L.; Chiu, H.-C.; Carpenter, A. E.; Tonks, I. A. Carbonylative Co- and Terpolymerizations of 10-Undecen-1-ol: A Route to Poly-

ketoesters with Tunable Compositions. *ACS Catal.* **2022**, *12*, 14629−14636.

(32) Čamdžić, L.; Stache, E. E. Controlled Radical Polymerization of Acrylates and Isocyanides Installs Degradable Functionality into Novel Copolymers. *J. Am. Chem. Soc.* **2023**, *145* (37), 20311−20318.

(33) Millich, F. Polymerization of Isocyanides. *Chem. Rev.* **1972**, *72* (2), 101−113.

(34) Cai, Z.; Ren, Y.; Li, X.; Shi, J.; Tong, B.; Dong, Y. Functional Isocyanide-Based Polymers. *Acc. Chem. Res.* **2020**, *53* (12), 2879−2891.

(35) Cahoon, C. R.; Bielawski, C. W. Metal-Promoted C1 Polymerizations. *Coordin Chem. Rev.* **2018**, *374*, 261−278.

(36) Saegusa, T.; Takaishi, N.; Ito, Y. Cationic Isomerization and Oligomerization of Isocyanide. *J. Org. Chem.* **1969**, *34* (12), 4040−4046.

(37) Hagiwara, S.; Takizawa, T.; Yamamoto, I. Polymerization of Isonitriles. *Chem. J. Japan* **1966**, *87* (12), 1355−1359.

(38) Liu, N.; Zhou, L.; Wu, Z.-Q. Alkyne-Palladium(II)-Catalyzed Living Polymerization of Isocyanides: An Exploration of Diverse Structures and Functions. *Acc. Chem. Res.* **2021**, *54* (20), 3953−3967.

(39) Liu, N.; Gao, R.-T.; Wu, Z.-Q. Helix-Induced Asymmetric Self-Assembly of π-Conjugated Block Copolymers: From Controlled Syntheses to Distinct Properties. *Acc. Chem. Res.* **2023**, *56*, 2954−2967.

(40) Zhou, L.; He, K.; Kang, S.-M.; Zhou, X.-Y.; Zou, H.; Liu, N.; Wu, Z.-Q. Photoswitchable Enantioselective and Helix-Sense Controlled Living Polymerization. *Angew. Chem., Int. Ed.* **2023**, *62* (52), No. e202310105.

(41) Xu, L.; Zhou, L.; Li, Y.-X.; Gao, R.-T.; Chen, Z.; Liu, N.; Wu, Z.-Q. Thermo-responsive chiral micelles as recyclable organocatalyst for asymmetric Rauhut-Currier reaction in water. *Nat. Commun.* **2023**, *14*, 7287.

(42) Kanbayashi, N.; Okamura, T.-A.; Onitsuka, K. Living Cyclocopolymerization through Alternating Insertion of Isocyanide and Allene via Controlling the Reactivity of the Propagation Species: Detailed Mechanistic Investigation. *J. Am. Chem. Soc.* **2019**, *141* (38), 15307−15317.

(43) Kanbayashi, N.; Yamamoto, R.; Okamura, T.-A.; Onitsuka, K. Living Cyclocopolymerization via Alternating Insertion of Alkyl Isocyanide and Allene to the Organonickel Complex. *Macromolecules* **2023**, *56* (21), 8658−8665.

(44) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. Living Radical Polymerization of Acrylates by Organocobalt Porphyrin Complexes. *J. Am. Chem. Soc.* **1994**, *116* (17), 7943−7944.

(45) Li, S.; Bruin, B. D.; Peng, C.-H.; Fryd, M.; Wayland, B. B. Exchange of Organic Radicals with Organo- Cobalt Complexes Formed in the Living Radical Polymerization of Vinyl Acetate. *J. Am. Chem. Soc.* **2008**, *130* (40), 13373−13381.

(46) Debuigne, A.; Poli, R.; Jerome, C.; Jerome, R.; Detrembleur, C. Overview of cobalt-mediated radical polymerization: Roots, state of the art and future prospects. *Prog. Polym. Sci.* **2009**, *34* (3), 211−239.

(47) Dadashi-Silab, S.; Stache, E. E. A Hydrometalation Initiation Mechanism via a Discrete Cobalt- Hydride for a Rapid and Controlled Radical Polymerization. *J. Am. Chem. Soc.* **2022**, *144* (29), 13311−13318.

(48) Lefay, C.; Guillaneuf, Y. Recyclable/degradable materials via the insertion of labile/cleavable bonds using a comonomer approach. *Prog. Polym. Sci.* **2023**, *147*, 101764.

(49) Yamago, S.; Miyazoe, H.; Goto, R.; Hashidume, M.; Sawazaki, T.; Yoshida, J. Synthetic and Theoretical Studies on Group-Transfer Imidoylation of Organotellurium Compounds. Remarkable Reactivity of Isonitriles in Comparison with Carbon Monoxide in Radical-Mediated Reactions. *J. Am. Chem. Soc.* **2001**, *123* (16), 3697−3705.

(50) Ryu, I.; Sonoda, N.; Curran, D. P. Tandem Radical Reactions of Carbon Monoxide, Isonitriles, and Other Reagent Equivalents of the Geminal Radical Acceptor/Radical Precursor Synthon. *Chem. Rev.* **1996**, *96*, 177−194.

(51) Minozzi, M.; Nanni, D.; Spagnolo, P. Imidoyl Radicals in Organic Synthesis. *Curr. Org. Chem.* **2007**, *11* (15), 1366−1384.

(52) Lei, J.; Huang, J.; Zhu, Q. Recent Progress in Imidoyl Radical-Involved Reactions. *Org. Biomol. Chem.* **2016**, *14* (9), 2593−2602.

(53) Sharma, S.; Pandey, A. P.; Sharma, A. Photocatalytical and Photochemical Generation of Imidoyl Radicals: Synthetic Applications. *Adv. Synth. Catal.* **2020**, *362* (23), 5196−5218.

(54) Lee, Y.; Boyer, C.; Kwon, M. S. Photocontrolled RAFT polymerization: past, present, and future. *Chem. Soc. Rev.* **2023**, *52*, 3035.

(55) Beres, M. A.; Rho, J. Y.; Kerr, A.; Smith, T.; Perrier, S. Photoiniferter-RAFT polymerization mediated by bis(trithiocarbonate) disulfides. *Polym. Chem.* **2024**, *15*, 522.

(56) Hartlieb, M. Photo-Iniferter RAFT Polymerization. *Macromol. Rapid Commun.* **2022**, *43*, 2100514.

(57) Merle, Y.; Merle-Aubry, L.; Guillet, J. E. Photolysis of Poly(acrylic acid) Containing an Aryl Ketone Chromophore. *Macromolecules* **1984**, *17* (3), 288−292.

(58) McKenzie, T. G.; Costa, L. P.; Fu, Q.; Dunstan, D. E.; Qiao, G. G. Investigation into the photolytic stability of RAFT agents and the implications for photopolymerization reactions. *Polym. Chem.* **2016**, *7*, 4246−4253.

(59) Sims, M. B.; Lessard, J. J.; Bai, L.; Sumerlin, B. S. Functional Diversification of Polymethacrylates by Dynamic β-Ketoester Modification. *Macromolecules* **2018**, *51*, 6380−6386.

(60) Qi, P.; Chen, H. L.; Nguyen, H. T. H.; Lin, C.-C.; Miller, S. A. Synthesis of biorenewable and water-degradable polylactam esters from itaconic acid. *Green Chem.* **2016**, *18*, 4170−4175.

(61) Ali, M. A.; Tateyama, S.; Oka, Y.; Kaneko, D.; Okajima, M. K.; Kaneko, T. Syntheses of High-Performance Biopolyamides Derived from Itaconic Acid and Their Environmental Corrosion. *Macromolecules* **2013**, *46*, 3719−3725.

(62) Conix, A.; Smets, G. Ring opening in lactam polymers. *J. Polym. Sci.* **1955**, *15*, 221−229.

(63) Vrancken, M.; Smets, G. Polymers and group interactions. I. Synthesis of polyampholytes. *J. Polym. Sci.* **1954**, *14*, 521−534.

(64) Vandenbrande, J. A.; Brown, J. R.; Arrington, A. S.; Long, T. E. Water-soluble polymers. In *Encyclopedia of Polymer Science and Technology*; Wiley, 2023. DOI: .

(65) Williams, P. A. *Handbook of Industrial Water Soluble Polymers*; Wiley, 2008.

(66) Bayliss, N.; Schmidt, B. V. K. J. Hydrophilic polymers: Current trends and visions for the future. *Prog. Polym. Sci.* **2023**, *147*, 101753.

(67) Future Market Insights (FMI). *Super Absorbent Polymer (SAP) Market—global Industry Analysis, Size And Forecast*. https://www.futuremarketinsights.com/reports/super-absorbent-polymer-market, 2020.

(68) Chazovachii, P. T.; Somers, M. J.; Robo, M. T.; Collias, D. I.; James, M. I.; Marsh, E. N. G.; Zimmerman, P. M.; Alfaro, J. F.; McNeil, A. J. Giving superabsorbent polymers a second life as pressure-sensitive adhesives. *Nat. Commun.* **2021**, *12*, 4524.

(69) Khoo, S. C.; Phang, X. Y.; Ng, C. M.; Lim, K. L.; Lam, S. S.; Ma, N. L. Recent technologies for treatment and recycling of used disposable baby diapers. *Process Saf. Environ. Prot.* **2019**, *123*, 116−129.

(70) Chazovachii, P. T.; Somers, M. J.; Robo, M. T.; Collias, D. I.; James, M. I.; Marsh, E. N.; Zimmerman, P. M.; Alfaro, J. F.; McNeil, A. J. Giving superabsorbent polymers a second life as pressure-sensitive adhesives. *Nat. Commun.* **2021**, *12*, 4524.

(71) Li, S.; Scheiger, J. M.; Wang, Z.; Huber, B.; Hoffmann, M.; Wilhelm, M.; Levkin, P. A. Diapers to Thickeners and Pressure-Sensitive Adhesives: Recycling of Superabsorbers via UV Degradation. *ACS Appl. Mater. Interface* **2023**, *15*, 44186.

(72) Jackson, A. W.; Mothe, S. R.; Ang, P.; Chennamaneni, L. R.; Herk, A. M. V.; Thoniyot, P. Backbone degradable poly(acrylic acid) analogue via radical ring-opening copolymerization and enhanced biodegradability. *Chemosphere* **2022**, *293*, 133487.

(73) Korpusik, A. B.; Adili, A.; Bhatt, K.; Anatot, J. E.; Seidel, D.; Sumerlin, B. S. Degradation of Polyacrylates by One-Pot Sequential Dehydrodecarboxylation and Ozonolysis. *J. Am. Chem. Soc.* **2023**, *145* (19), 10480−10485.