

Photo-Iniferter RAFT synthesis of versatile, non-alternating poly(acrylate-*co*-isocyanides)

Lejla Čamdžić, §,† Erin E. Stache*§

§Department of Chemistry, Princeton University, Princeton, New Jersey 08544, United States

†Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, United States

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ABSTRACT: Non-alternating poly(isocyanide-*co*-acrylate) copolymers enable access to novel polymer microstructures with versatile chemistry and allow for designed mechanical properties, an important facet of combatting 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 polyacrylic acid-like copolymers with small amounts of ketone linkages through hydrolysis, enabling faster degradation rates for this class of polymer.

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 towards developing and adopting new materials is imperative. These materials must not only replicate the functionalities of existing plastics but also prioritize sustainability, biodegradability, and reduced environmental impact.⁵⁻⁹ Carbonyl-containing polymers are of great interest due to their susceptibility to photodegradative pathways under ultraviolet light irradiation, such as Norrish cleavages.¹⁰⁻¹³ Introducing minimal carbonyl content facilitates breakdown in the environment and maintains parent physical properties; however, realizing such commercial materials has proven difficult.¹⁴⁻²⁶

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 non-alternating poly(isocyanides-*co*-acrylates) (Scheme 1).²⁷⁻³² Implementing a reversible deactivation radical polymerization (RDRP) attenuated unproductive termination and chain transfer events and provided control over polymer molecular weights and dispersity.³³⁻³⁶ 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 non-alternating 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.³⁷

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.³⁸⁻⁴² 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.

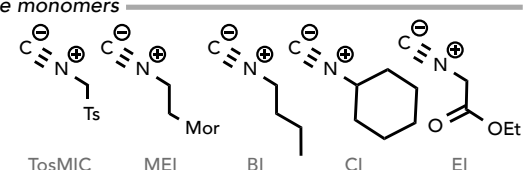
To expand the scope and applicability of the copolymerization of isocyanides, we sought to use photo-iniferter reversible addition-fragmentation chain transfer (PI-RAFT) (Scheme 1).⁴³⁻⁴⁵ Using light for initiation offers spatiotemporal regulation over the polymerization without exogenous photocatalysts. 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 poly lactams and photodegradable water-soluble materials.⁴⁶

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]. Theoretical incorporation (Inc.^{theo}) is calculated based on monomer conversion (see supporting information for more details). Molecular weight values are in kg/mol.

We explored various isocyanides to expand the comonomer scope and compare the effect of different electronic and structural properties (Figure 1). In addition to TosMIC and MEI, *n*-butyl isocyanide (BI) and cyclohexyl isocyanide (CI), along with ethyl isocyanoacetate (EI), were copolymerized with good control. In contrast, the aromatic 4-methoxyphenyl isocyanide (MPI) was unsuccessful, not reaching sufficient conversion in the same timeframe. Electron-donating substituents lead to an increase in incorporation, while the steric bulk seems to be a hindrance to efficient polymerization.

Isocyanide monomers



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

Figure 1. Scope of isocyanides successfully copolymerized with MA.

Kinetic analysis of the monomer conversions of the MA-TosMIC copolymerization initially showed linear 1st-order kinetics (see supporting information for more details). 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 2a).

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 re-initiation and controlled chain extension with good chain end fidelity, which we calculated to be 84 % from the residual unreacted chains (Figure 2b). The copolymer synthesized from MEI exhibited slightly better chain end fidelity than those synthesized using TosMIC (see supporting information for more details).

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 2c). Monomer conversion and molecular weight growth were only seen when the light was turned on, and dispersities remained low throughout.

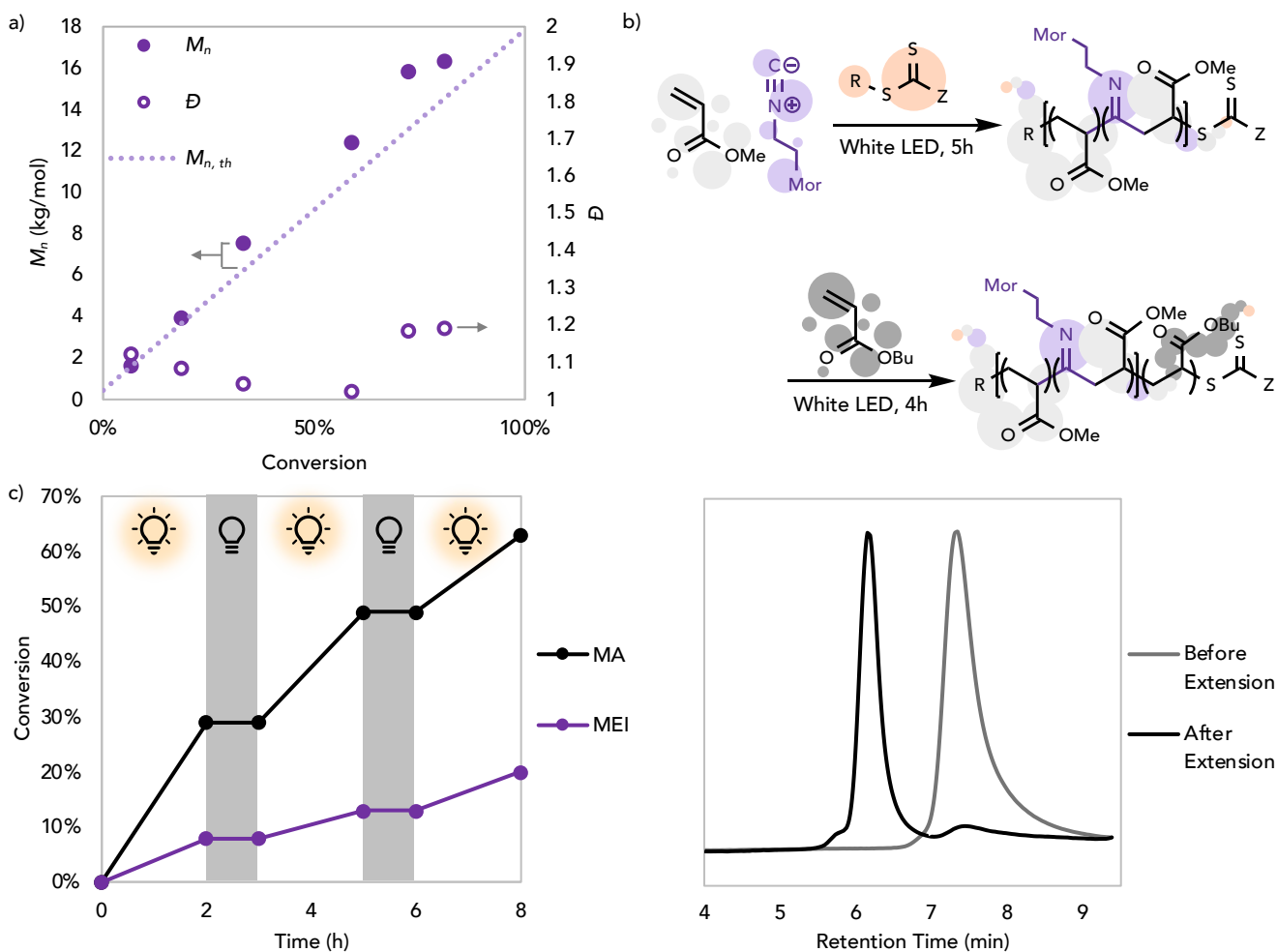


Figure 2. a) Molecular weight plotted against the averaged conversion of MA and MEI via PI-RAFT. b) Chain extension of poly(MA-co-MEI) copolymers with nBA. c) Plot of monomer conversion over time as the light is turned on and off periodically throughout the polymerization.

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 ^1H NMR around 3.7 ppm, 3.5 ppm, 2.7 ppm, 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, EI, and CI copolymers also exhibit protons near 9.4 ppm indicating tautomerization to the enamine. The MEI, BI, and EI copolymers exhibit two proton signals, signifying an enamine. Through ^1H - ^{15}N HSQC and ^1H - ^{13}C HMBC 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 more 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 at 9.4 ppm, which correlates to a nitrogen with a chemical shift (47 ppm) similar to that of amines from ^1H - ^{15}N heteronuclear single quantum coherence (HSQC) nuclear magnetic resonance (NMR) experiments (Figure 3).⁴⁷ Excitingly, we see the appearance of a proton signal slightly downfield at 10 ppm that, from ^1H - ^{15}N HSQC and ^1H - ^{13}C heteronuclear multiple bond coherence (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 3). We observe this to occur slowly over time in solution, presumably in the presence of adventitious water. 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.⁴⁸⁻⁵¹ Significantly, pyrrolidone-containing polylac-

tams 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 gen-

erate these materials. 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.

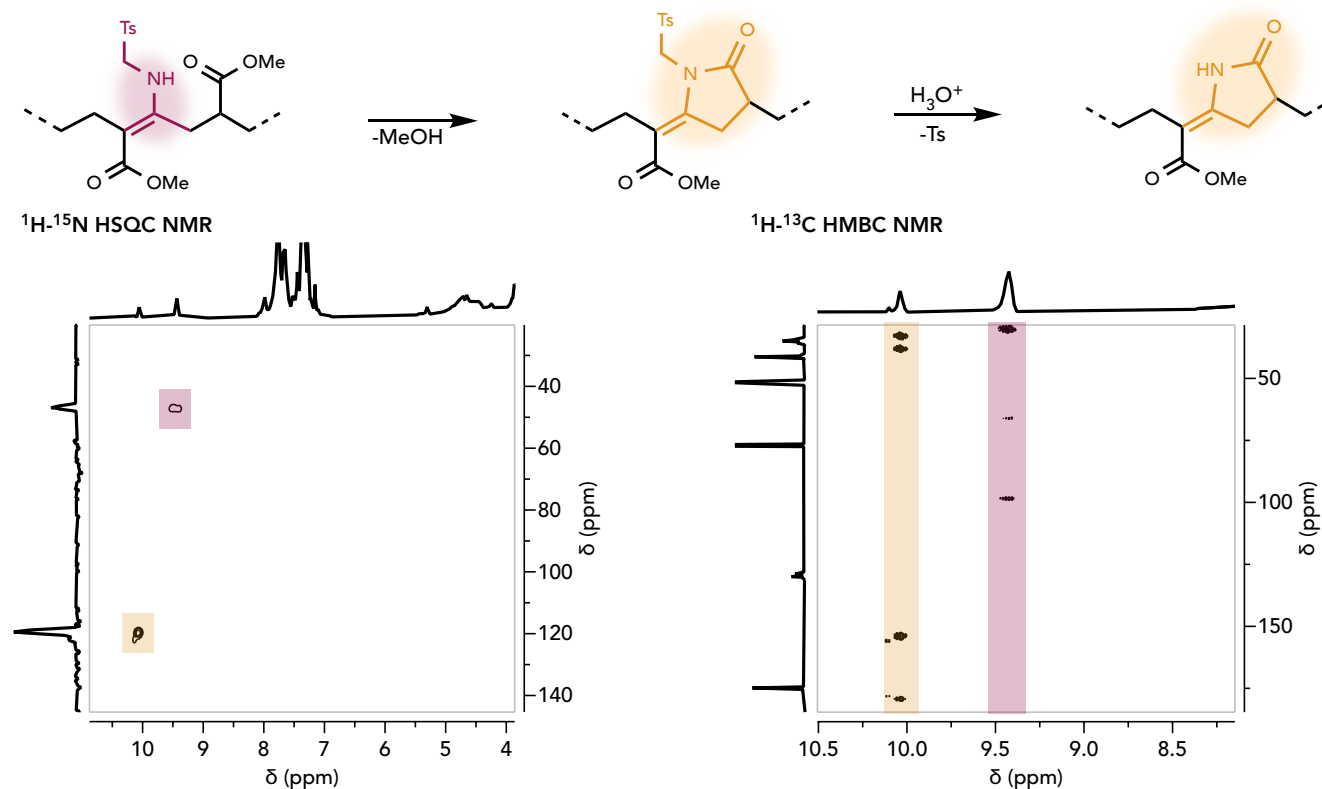


Figure 3. Evidence of lactamization of poly(MA-co-TosMIC) through 1H - ^{15}N HSQC and 1H - ^{13}C HMBC NMR experiments.

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 4). We then sought to fully hydrolyze these copolymers to poly(acrylic acid)-like polymers under more forcing conditions. Polyacrylic acids (PAA) and sodium polyacrylate-based materials are synthetic polymers known for their water-absorbing and adhesive properties,⁵²⁻⁵⁴ with an estimated annual production of around 2 million metric tons.⁵⁵ However, PAA is challenging to recycle or degrade due to the difficulty of removal from the environment and its stable molecular structure.⁵⁶⁻⁵⁹ Through our conditions, these poly acrylic acid-like materials will have embedded photodegradable carbonyl linkages, offering a degradable pathway for this class of polymers.⁶⁰ Using conditions previously reported by the Sumerlin group,⁶¹ the rate of hydrolysis of the homopolymers was first studied. Homopolymers of *t*-butyl acrylate hydrolyzed quickest, followed by MA and phenyl acrylate (see supporting information for more details). 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 non-alternating poly(acrylic

acid-co-ketones) (see supporting information for more 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.

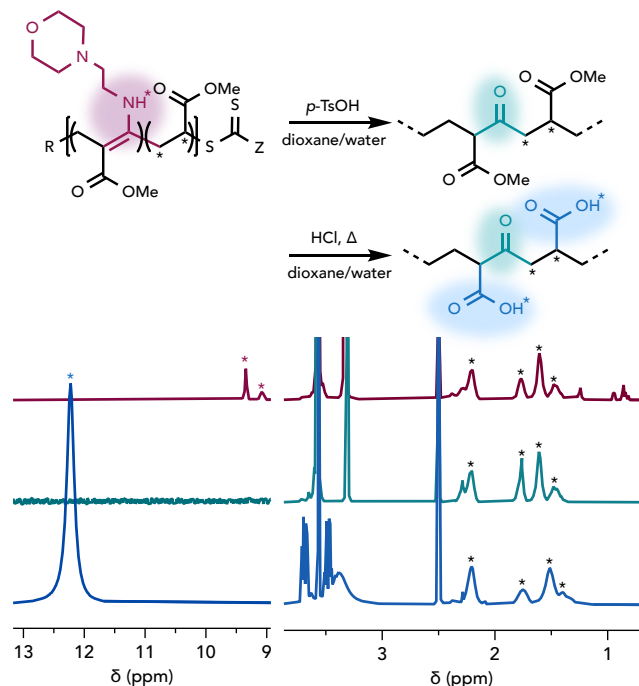


Figure 4. Sequential hydrolysis of multiple microstructures. Overlaid spectra from 9–13 ppm are on different scales to clearly distinguish peaks at different chemical shifts.

Lastly, the introduction of ketones to poly acrylic acid enabled photodegradation. Upon irradiation with 390 nm light, the degradation of the non-alternating 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 (see supporting information for more details). Because these water-soluble polymers cannot be reclaimed from the environment, installing this photodegradable linkage is a potential means of breaking down these materials.

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 non-accumulative waste stream.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Details of experimental procedures and additional supplementary results (PDF)

AUTHOR INFORMATION

Corresponding Author

* **Erin E. Stache** – Department of Chemistry, Princeton University, Princeton, New Jersey 08544, United States; ORCID: 0000-0002-4670-9117

Email: estache@princeton.edu

Author

§ **Lejla Čamdžić** – Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, United States; ORCID: 0000-0001-9234-6030

Present Addresses

§ Department of Chemistry, Princeton University, Princeton, New Jersey 08544, United States

Notes

The authors declare no competing financial interests.

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