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Controlled Radical Polymerization of Acrylates and Isocyanides Installs Degradable Functionality into Novel Copolymers

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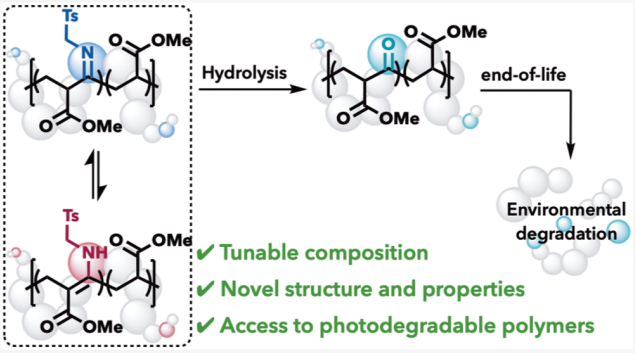
ABSTRACT: Installing ketones into a polymer backbone is a known method for introducing photodegradability into polymers; however, most current methods are limited to ethylene−carbon monoxide copolymerization. Here we use isocyanides in place of carbon monoxide in a copolymerization strategy to access degradable nonalternating poly(ketones) that either maintain or enhance the thermal properties. A cobalt-mediated radical polymerization of acrylates and isocyanides synthesizes nonalternating poly(acrylate-*co*-isocyanide) copolymers with tunable incorporation using monomer feed ratios. The kinetic product of the polymerization is a dynamic β-imine ester that tautomerizes to the β-enamine ester. Hydrolysis of this copolymer affords a third copolymer microstructure—the elusive nonalternating poly(ketone)—from a single copolymerization strategy. Analysis of the copolymer properties demonstrates tunable thermal properties with the degree of incorporation. Finally, we show that poly(acrylate-*co*-isocyanide) and poly(acrylate-*co*-ketone) are photodegradable with 390 nm light, enabling chain cleavage.



INTRODUCTION

Degradable and reusable plastics are essential for mitigating consequences from the disproportionate rate of plastic waste production to plastic degradation or recycling.[1−3] Of immense interest is a strategy that programs degradable functionality into the polymer microstructure while maintaining functional polymer properties.[4−7] Poly(ketones), the alternating copolymers of vinyl monomers and carbon monoxide (CO), are of longstanding significance due to their enhanced thermal properties and inherent degradability via Norrish cleavage reactions.[8−18] Decades of research have focused on catalyst design for controlling these polymerizations. More recently, research has focused on incorporating low percentages of ketone functionality into the backbone of polyethylene, which has been shown to introduce degradability without dramatically altering the physical properties.[19] However, this strategy has only been effective for ethylene monomer using coordination polymerizations, leaving other monomers underexplored (Scheme 1).[20−24]

An alternative approach to this goal is radical copolymerization with CO, which renders the CO incorporation tunable with monomer composition.[25−27] However, the rapid decarbonylation reaction with activated monomers inhibits the utility of this approach unless under exceedingly high pressures of CO, again limiting the success to ethylene copolymerizations (Scheme 1). Additionally, control over the copolymer microstructure is limited due to the reactive acyl radical, which can undergo intramolecular hydrogen atom transfer (i.e., 1,5-HAT), causing branching and chain transfer. New polymerization strategies are necessary to access and use this polymer class more broadly.[28] Isocyanides are an attractive isoelectronic alternative to CO that are easy to handle and electronically tunable through synthesis from inexpensive starting materials.[29] Isocyanides have been thoroughly investigated as a class of C_1 monomers that form poly(isocyanides) through a transition-metal-catalyzed polymerization.[30−35]

Importantly, isocyanides can undergo radical addition analogously to CO with more precise stoichiometry and lower rates of α-scission.[36] To investigate the viability of copolymerizing isocyanides, we envisioned radical copolymerization with a more activated acrylate monomer to reveal poly(acrylates-*co*-isocyanides) (Scheme 1). The polymer sequence could be tuned by adjusting the monomer stoichiometry. Ultimately, hydrolysis would afford nonalternating poly(acrylates-*co*-ketones), elusive copolymers with degradable ketones within the backbone.

Despite the potential opportunities afforded through nonalternating incorporation of isocyanides, these monomers have

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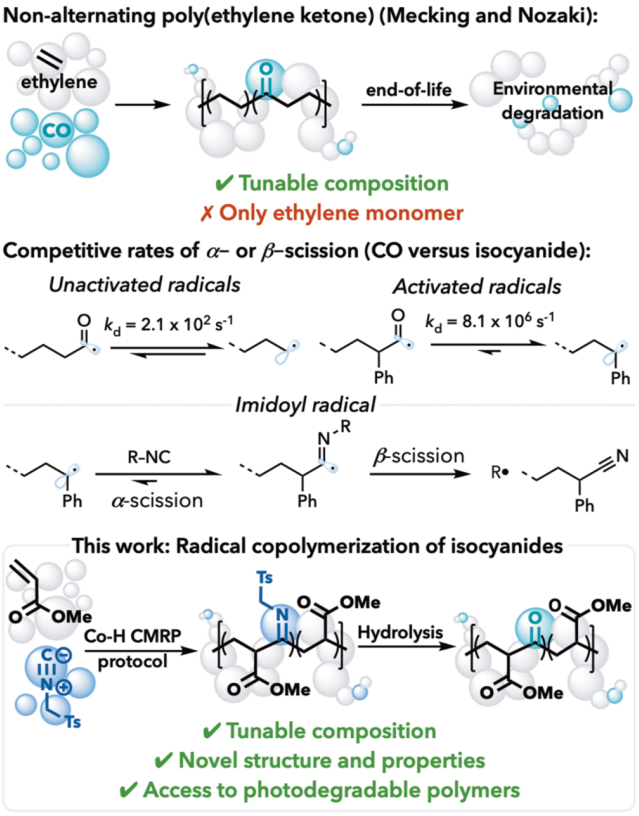
Scheme 1. Inclusion of Ketones in Copolymers for Degradability and Novel Approach Using Isocyanides to Access Degradable Polymers



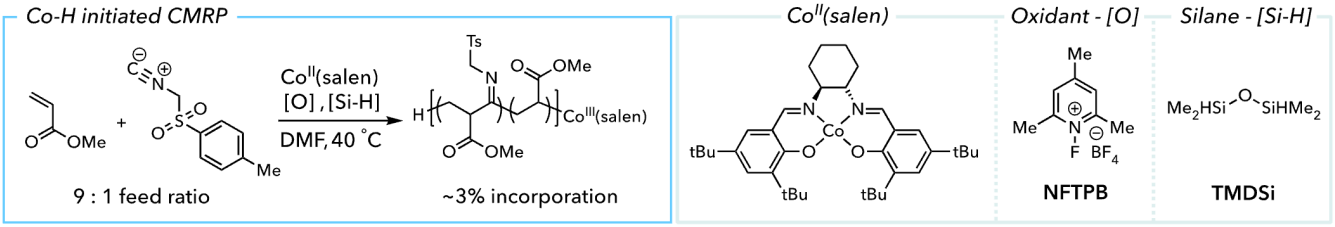
not been leveraged in radical copolymerization.[36−42] The use of free radical polymerization methods offers a facile way to generate the desired copolymer. However, a major potential challenge lies in the reactive imidoyl radical, which can undergo competitive β-scission to form nitriles as well as hydrogen atom abstraction leading to polymer branching and incorporation on side chains rather than within the polymer backbone.[43] With the eventual degradation of our copolymer in mind, incorporation of the isocyanide via undiverted radical propagation is necessary to have meaningful cleavages of the polymer backbone.

We envisioned that implementing a reversible-deactivation radical polymerization (RDRP) would decrease the radical concentration, reducing unproductive termination and chain transfer events and giving control over molecular weight and dispersity. A cobalt-mediated radical polymerization (CMRP) is ideally suited for RDRP of both activated and less activated monomers due to the weak Co−C bond, allowing for future expansion to different monomer classes.[44−47] We hypothesized that a judicious choice of cobalt complex would reversibly terminate the imidoyl radical, facilitating control over polymer molecular weight and dispersity in a complementary fashion to free radical polymerization. Here we describe a controlled radical polymerization of isocyanides with acrylates for programming degradable functionality into poly(acrylates).

RESULTS AND DISCUSSION

Free Radical Polymerization. We began our studies using azobis(isobutyronitrile) (AIBN) to initiate the free radical copolymerization of methyl acrylate (MA) and *p*-tosylmethyl isocyanide (TosMIC) (Table 1). The starting ratio of comonomers was chosen to target low but significant incorporation of 3% isocyanide. Using a 9:1 feed ratio of MA to TosMIC, we were able to isolate poly(MA-*co*-TosMIC) with 3% incorporation (PMAT-3) with a broad polymer molecular weight distribution (Table 1, entry 1). The incorporation of isocyanides into the backbone and new copolymer structure was confirmed by detailed NMR analysis.

Table 1. Co−H-Initiated Cobalt-Mediated Radical Polymerization of MA and TosMIC[a]



entry[b]	deviation	DP	MA/TosMIC conversion (%)	$M_{n,th}$ (kg/mol)[c]	M_n (kg/mol)	$Đ$	incorporation (%) exp[d]	incorporation (%) theor[e]
1[f]	free radical	–	84/44	–	11.2	2.49	3.2	5.5
2	–	100	37/28	4.0	4.3	1.21	3.2	7.6
3	–	200	37/20	7.2	8.6	1.22	2.6	5.6
4	–	400	45/20	16.1	17.2	1.49	2.5	4.7
5	–	600	56/26	29.7	27.4	1.51	2.5	4.9
6[g]	conventional CMRP	100	12/53	2.6	2.9	1.51	3.7	33.6
7[h]	TosMIC added at Co^{II}	100	65/43	6.5	9.0	1.71	3.1	6.8
8[i]	no Co^{II}	–	61/45	–	–	–	–	–

[a]Oxidant = *N*-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (NFTPB), silane = 1,1,3,3-tetramethyldisiloxane (TMDSi), reaction time = 2 h; TosMIC added 5 min after silane. [b][Monomer]/[Co]/[NFTPB]/[TMDSi] = DP/1/0.55/0.5. [c]Theoretical number-average molecular weight, $M_{n,th}$ = ([MA]/[Co] × MA conversion × M_{MA}) + ([TosMIC]/[Co] × TosMIC conversion × M_{TosMIC}) + $M_{Co(Ln)}$. [d]TosMIC incorporation calculated from ^{1}H NMR analysis of precipitated sample. [e]Theoretical incorporation calculated based on monomer conversion. [f][MA]/[TosMIC]/[AIBN] = 90/10/5 at 60 °C. [g][MA]/[TosMIC]/[AIBN]/[Co] = 90/10/5/1 at 60 °C for 5 h. [h]TosMIC was added initially. [i]Cobalt was omitted.

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It is important to note that no polymerization of TosMIC occurred in the absence of MA.

We sought to study the copolymerization kinetics to resolve the monomer distribution and composition of the resultant copolymers. We experimentally determined the relative reactivity ratios of TosMIC to MA by performing a series of copolymerizations with varied starting concentrations of the monomers. Using the Mayo–Lewis model, the relationship between the starting monomer mole fractions (f_{MA} and f_T, where $f_{MA} + f_T = 1$) and the instantaneous copolymer composition (F_{MA} and F_T, where $F_{MA} + F_T = 1$) at low monomer conversion affords the reactivity ratios, r (where k_{x-Y} represents the propagation rate of Y monomer to x radical). Given previous studies with the analogous acyl radical, we assume that the corresponding *N*-acyl radical does not homopropagate.[19] Because consecutive radical insertions of TosMIC are assumed to be nonexistent, the copolymerization parameter for TosMIC becomes $r_T = 0$. This assumption simplifies the copolymerization equation (eq 1):

$$F_{MA} = \frac{r_{MA}f_{MA}^{\ 2} + f_{MA}f_T}{r_{MA}f_{MA}^{\ 2} + 2f_{MA}f_T} \text{ where } r_{MA} = \frac{k_{ma-MA}}{k_{ma-T}} \quad (1)$$

A Mayo–Lewis plot was generated to provide an initial indication of the copolymer composition as a function of feed ratio (Figure 1). The portion of MA in the copolymer is higher

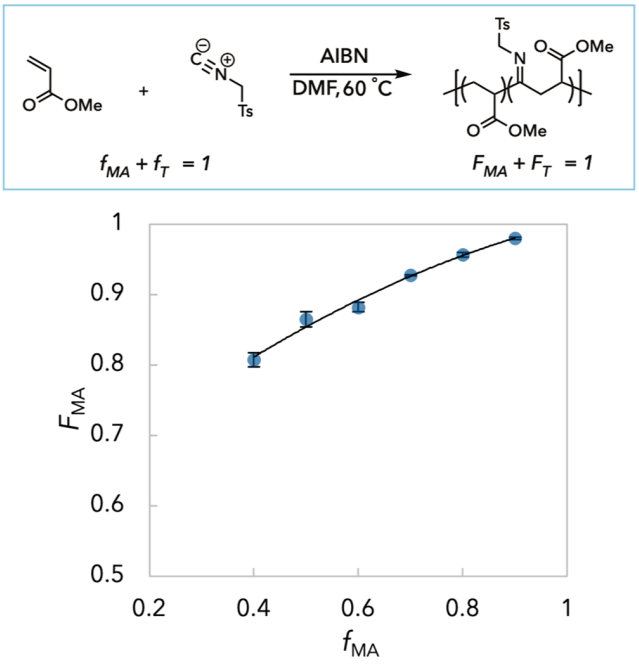

Figure 1. Mayo–Lewis plot of the mole fraction of MA in the instantaneous copolymer, F_{MA}, versus the mole fraction of MA in the starting monomer concentration, f_{MA}.

than the monomer feed ratio for all starting monomer compositions, suggesting that MA incorporation is favored over TosMIC incorporation. From these data, the r_{MA} value at 60 °C was determined to be 5.2. This agrees with the r_{MA} values of 5.2 and 4.8 obtained using the Fineman–Ross and Kelen–Tüdös methods, respectively (see the Supporting Information for more details).[48]

Favorable incorporation of one monomer over the other often leads to a compositional drift in copolymers. To verify the impact of this in our polymer microstructure, a series of copolymerizations were allowed to proceed to high conversion, and the final composition was examined. The incorporation of TosMIC remained consistent throughout the polymerization, supporting a random copolymer structure with minimal effect from compositional drift, which is important to maximize the effect of chain cleavages from the degradable moiety (Figure S3).

Cobalt-Mediated Radical Polymerization. Next, we decided to explore the use of CMRP for a controlled radical polymerization.[47] When implementing CMRP, we recognized that isocyanides strongly ligate to Co(II), which could result in unwanted monomer reactivity with the metal complex rather than copolymerization.[49] We recently disclosed a novel CMRP method utilizing a cobalt–hydride (Co–H) initiator to rapidly initiate and control the polymerization of acrylates and acrylamides.[50] In our protocol, oxidation of Co(II) to Co(III) followed by treatment with silane affords Co(III)–H, which rapidly hydrometalates monomer to initiate polymerization. The polymerization proceeds rapidly at mild temperatures with excellent molecular weight and dispersity control. We hypothesized that this rapid initiation protocol would reduce the overall Co(II) concentration, thereby avoiding reactions of isocyanides with cobalt, and the polymerization would proceed under mild conditions.

Excitingly, implementation of Co–H-initiated CMRP with the same initial ratio of 9:1 afforded PMAT-3 after just 2 h at 40 °C (Table 1, entry 2). The low dispersity and close agreement between experimental and theoretical molecular weights (M_n) demonstrate control over the polymerization process. Furthermore, higher degrees of polymerization of 200, 400, and 600 were targeted with a corresponding increase in molecular weight while maintaining a consistent degree of incorporation (Table 1, entries 3–5). There is a small discrepancy between the theoretical and experimental TosMIC incorporations, which notably decreases with increasing DP.

Conventional CMRP, using Co(II) with radical initiators, has long induction periods, which prolong the isocyanide interaction with free Co(salen) and would likely limit control over the polymerization. Using conventional CMRP, we observed decreased MA conversion, and unproductive conversion of TosMIC increased, as low incorporation was maintained in the isolated polymer (Table 1, entry 6). We hypothesized that isocyanide ligation to Co(II) at elevated temperatures inhibited radical polymerization and promoted side reactions. We explored this effect using our Co–H protocol by adding TosMIC before the oxidation of the cobalt complex (Table 1, entry 7; see the Supporting Information for more details). While this protocol did not result in a large degree of unproductive TosMIC conversion, control over the molecular weight was less efficient, and the dispersity increased. The fast Co–H generation and subsequent hydrometalation likely limited isocyanide interaction with the cobalt complex. Notably, no polymerization occurred when cobalt was omitted from the reaction (Table 1, entry 8). These results highlight the utilization of Co–H species to rapidly hydrometalate and initiate and maintain control over the copolymerization of acrylates with isocyanides.

To further confirm the radical mechanism of polymerization, a radical scavenger (TEMPO) was added to the reaction mixture after 30 min. We observed polymerization inhibition with no monomer conversion or M_n increase (Figure S7). Additionally, no polymerization was observed with the cobalt

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complex only, precluding a transition metal insertion mechanism.

We sought to examine the kinetics of copolymerization using a Co−H-initiated CMRP and monitored the polymerization over time. Our conditions show linear semilogarithmic kinetic behavior of both monomers with slower conversion of TosMIC relative to MA (see Figures S8 and S9). The observed rate constants for MA and TosMIC were calculated as k_{MA} = 0.104 h^{-1} and k_{TosMIC} = 0.029 h^{-1}. Typically, in a copolymerization of two monomers with different reactivity ratios, after significant consumption of the first monomer, an increase in conversion is observed for the second monomer.[51] This phenomenon is not observed in this system, further supporting our hypothesis that TosMIC will not homopropagate and compositional drift is minimal, as observed in our free radical polymerization studies. Indeed, the polymerization dramatically slows as MA is consumed, and the concentration of TosMIC increases relative to propagating chains. Further, the composition of the copolymer stays consistent throughout the polymerization, supporting a random copolymer structure.

The molecular weights increase linearly with conversion and are in agreement with the theoretical M_n, showing good control under these conditions (Figure 2). The dispersity

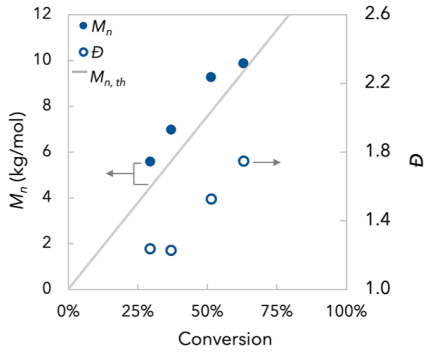
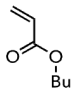
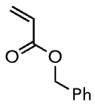
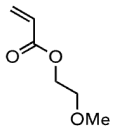
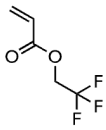


Figure 2. Linear evolution of M_n (solid points, left y axis) and dispersity (open points, right y axis) per total monomer conversion in the copolymerization of MA and TosMIC with a Co−H-initiated CMRP protocol.

remains low up to 50 and 30% conversion of MA and TosMIC, respectively. We found that the dispersity increases at higher conversion. This could be a consequence of 1,5-HAT typically found in radical polymerizations of acrylates. We hypothesized that the introduction of the isocyanide would result in increased levels of β-scission of the imidoyl radical as well as 1,5-HAT at higher conversions and/or equivalents as the polymerization rate decreases. Interestingly, 1,4-HAT resulting in a more stable tertiary radical could also be of consequence. However, NMR analysis did not conclusively support any of these structures (Figure S27). Additionally, ligation of the β-imine ester in the polymer backbone may inhibit reversible deactivation of the propagating chain end by the cobalt mediator (see the Supporting Information).

We successfully applied this CMRP system to various other acrylate monomers, such as n-butyl acrylate (n-BA), benzyl acrylate (BnA), 2-methoxyethyl acrylate (MEA), and the fluorinated monomer 2,2,2-trifluoroethyl acrylate (TFEA) (Table 2). The copolymerizations proceeded with reasonable control over the molecular weight and dispersity. Interestingly, despite using a consistent 9:1 feed ratio, the isocyanide

Table 2. Scope of Acrylates Used as Comonomers[a]

Acrylate monomers				
	n-BA	BnA	MEA	TFEA
M / TosMIC Conv. (%)	45 / 32	59 / 43	51 / 37	51 / 41
$M_{n,th}$	6.4	10.0	7.3	8.5
M_n	8.9	10.4	8.0	10.3
Đ	1.22	1.29	1.27	1.20
Incorp. (%)	1.8	1.1	2.1	3.6

[a]Reaction conditions: [M]/[TosMIC]/[Co]/[NFTPB]/[TMDSi] = 90/10/1/0.55/0.5 in DMF (50 vol %) at 40 °C. M_n values are in kg/mol.

incorporation changed with the monomer, from 1.1% for BnA to 3.6% for TFEA. We hypothesize that the more electrophilic character of the radical from TFEA increases the cross-propagation rates with the nucleophilic isocyanide comonomer, resulting in slightly higher incorporation. However, further studies are needed to investigate reactivity ratios to fully correlate the degree of incorporation.

Copolymer Microstructure. A key advantage of our polymerization strategy is the facile ability to tune the polymer sequence and therefore optimize polymer properties and degradability, which we hypothesized would be affected by the degree of incorporation. We first employed our standard polymerization protocol but altered the monomer feed ratio from 9:1 to 2:8 MA to TosMIC. Gratifyingly, this enabled targeted degrees of isocyanide incorporation from 3% to 35% (Figure 3). Loss of control over molecular weight and

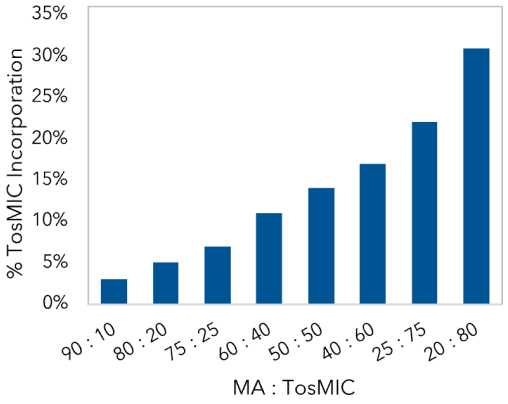


Figure 3. Tuning isocyanide incorporation with the monomer feed ratio.

broadened dispersity were observed with a gradual decrease in overall molecular weight with increasing TosMIC in the feed ratio. We suspect that at higher TosMIC loading, there is an increase in the prevalence of termination and chain transfer events.

We performed detailed NMR studies to support our hypothesized polymer microstructure. NMR analysis of the copolymer composition was challenging due to several possible

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conformations of the dynamic β-imine ester linkage and the novel nature of the polymer structure and isocyanide monomer. When determining the initial conformation of the copolymer, we identified the β-imine ester as the kinetic product of the polymerization, which could be isolated and maintained in the solid state under inert conditions (Figure 4). This is most notably shown in ^{1}H NMR by the singular peak at 4.7 ppm corresponding to the methylene protons between the nitrogen and sulfur atoms.

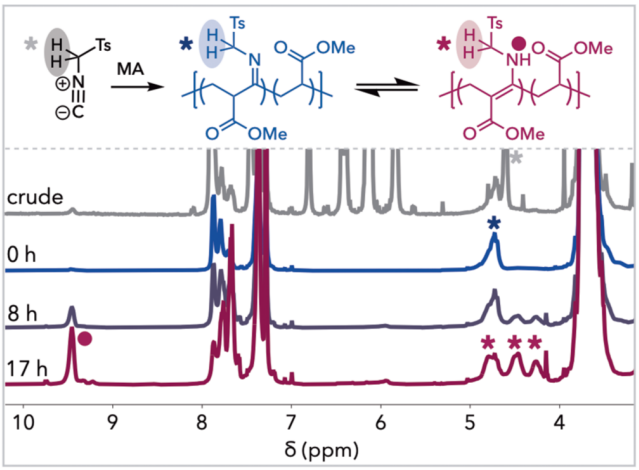

Figure 4. ^{1}H NMR analysis of tautomerization of the copolymers in $CDCl_3$.

Upon dissolution in protic solvents or prolonged exposure in ambient conditions, the copolymer tautomerizes to the β-enamine ester, a vinylogous urethane structure directly integrated into the polymer backbone.[52] The enamine conformation is the expected thermodynamically stable tautomer due to stabilization by formation of a pseudo-six-membered hydrogen-bonded ring, although there are several possible conformations to consider related to E/Z conformation around the double bond and also the C–N bond.[53,54] Analysis of the equilibrium of PMAT-3 in $CDCl_3$ over time shows significant tautomerization within 17 h at room temperature (Figure 4). This is seen by the splitting of the methylene peak into three peaks as well as the appearance of an enamine proton downfield at 9.4 ppm.

Excitingly, treatment of PMAT-3 with aqueous p-toluenesulfonic acid (p-TsOH) in dioxane resulted in nearly quantitative hydrolysis to form the elusive nonalternating poly(MA-*co*-ketone) (PMAK-3) (Figure 5a). This is evident by the disappearance of peaks corresponding to TosMIC and the appearance of carbon signals at 201–203 ppm, characteristic of carbonyls of β-keto esters (see the Supporting Information for more details). The simpler spectra of the hydrolyzed copolymers were useful in retroactively discerning the PMAT structure. Notably, the hydrolyzed copolymers synthesized via CMRP rather than free radical polymerization provided cleaner copolymer structures, with nearly complete loss of aromatic peaks. This leads us to hypothesize that the polymers synthesized by free radical polymerization are more susceptible to defects and side reactions, highlighting the use of CMRP for a cleaner polymerization. Careful 1D and 2D NMR analysis of the precipitated copolymer showed trace amounts (<0.1%) of chain-end aldehydes (arising from 1,5-HAT or intermolecular HAT/chain transfer) at higher TosMIC loadings (see Figure S79). Additionally, nitrile chain ends resulting from β-scission were below the limit of detection. All spectral data support the majority formation of in-chain β-enamine esters upon tautomerization and in-chain ketones upon polymer hydrolysis.

Thermal Properties. After accessing these new polymer microstructures with varied compositions using this single copolymerization method, we sought to examine the effect of the microstructure and composition on the thermal properties of the copolymers. Adding ketones into the polymer backbone has been shown to enhance the glass transition temperature (T_g) due to the introduction of an increased dipole.[13] We hypothesized that the β-enamine ester would afford an even higher T_g due to the increased steric bulk of the tosylmethyl group and the introduction of sp^2-hybridized carbons, which inhibit rotation of the polymer backbone. We further envisioned that increasing incorporation would be directly correlated with increases in T_g.

A series of copolymers with varying degrees of isocyanide incorporation (PMAT-3, -5, and -10) were synthesized and tautomerized to the β-enamine ester copolymers.[55] This series of copolymers were also hydrolyzed to afford the poly(ketones) with analogous incorporation (PMAK-3, -5, and -10). DSC analysis showed that the PMAT copolymers in the enamine conformation had dramatically enhanced thermal properties compared to PMA, which has a low T_g (8 °C). With

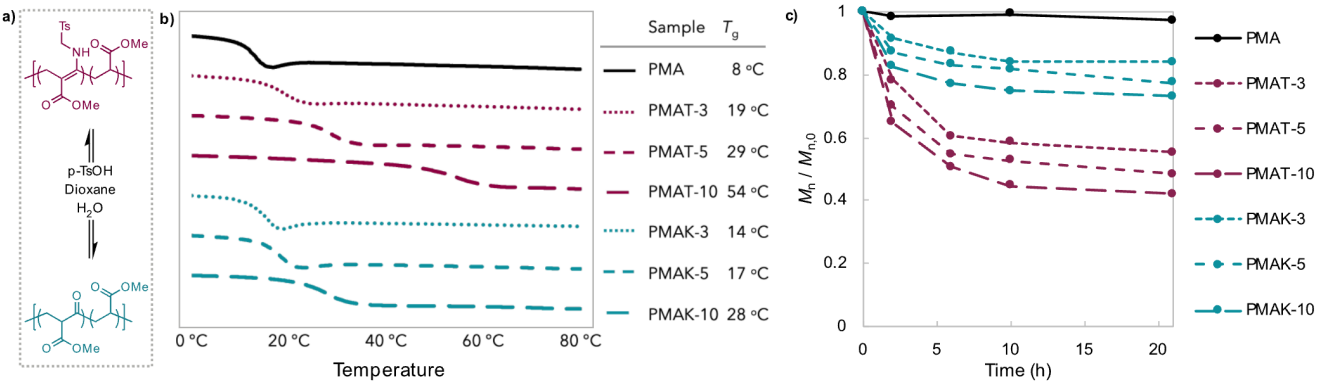

Figure 5. (a) Hydrolysis of poly(MA-*co*-isocyanide) (PMAT) to poly(MA-*co*-ketone) (PMAK). (b) DSC traces for a series of copolymers and comparison to PMA. (c) Change in molecular weights of PMA, PMAK-3, and PMAT-3 after 390 nm light irradiation in solution.

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3% TosMIC, the T_g increased to 19 °C (Figure 5b). With 5 and 10% incorporation, the T_g linearly increased to 29 and 54 °C, respectively. These results demonstrate the tunability in incorporation to affect the thermomechanical properties. Interestingly, the hydrolyzed copolymers containing ketone linkages displayed thermal properties intermediate between those of PMA and PMAT. For PMAK-3, a T_g of 14 °C was observed, with a modest increase to 17 and 28 °C for PMAK-5 and PMAK-10, respectively. Ultimately, the versatility and control over thermal properties are demonstrated through the degree of isocyanide incorporation and by accessing different microstructures in the polymer backbone, giving access to a broad range of T_g's from a single copolymerization.

Photodegradation. Finally, we studied the photodegradation properties of the copolymers with varying TosMIC incorporation (Figure 5c). Poly(ketones) are known to undergo photodegradation with intense UV light via Norrish cleavages. We hypothesized that the enamine-containing copolymers might also undergo photodegradation under mild irradiation conditions. When the copolymers were irradiated with near-visible 390 nm light in solution, the molecular weight of the poly(ketone) derivative decreased over time, analogously to previous reports with polyethylene, suggesting Norrish-type chain cleavage events (see the Supporting Information for more details).[19] Structural analysis of the material after irradiation via ^{13}C NMR showed a loss of carbonyl groups. Excitingly, the enamine-containing copolymer also underwent photodegradation with higher efficiency than the corresponding ketone. We observed a loss of peaks from TosMIC incorporation. Indeed, the extent of degradation correlated with the degree of included degradable moieties. Further studies are underway to understand the mechanism and degradation products from these copolymers. Notably, the PMA homopolymer was stable under irradiation due to the absence of the ketone or enamine functional groups. These initial studies suggest that the newly synthesized copolymers will undergo photodegradation analogous to previously synthesized poly(ketones), even under near visible-light irradiation.

CONCLUSIONS

In this work, we have described the tunable copolymerization of isocyanides and acrylates to produce novel copolymers using a cobalt-mediated radical polymerization with Co−H as a discrete and rapid initiator. Conformational interconversions of the backbone structure lend access to two unique copolymers, which can be further modified via hydrolysis to form a third—the corresponding nonalternating ketone. The inclusion of small amounts of the ketone functional group imparts similar thermal properties but enhanced photodegradability compared to the analogous homopolymer, even under near visible-light irradiation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c04595.

Details of experimental procedures and additional supplementary results (PDF)

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Notes

The authors declare the following competing financial interest(s): E.E.S. and L.C. are inventors on U.S. provisional letters patent application 10414:63/838,378, submitted by Cornell University, the status of which is pending, which covers the methods in this paper.

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