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Ring Opening Metathesis Polymerization of a New Monomer Derived from a Nitroso Diels–Alder Reaction

*Selesha Subnaik, Katya Sheridan, and Christopher E. Hobbs**

A nitroso Diels–Alder (NDA) reaction between cyclopentadiene and an in situ generated nitroso compound leads to a new heterocyclic monomer for ring opening metathesis polymerization (ROMP) reactions. This monomer could be polymerized in the presence of Grubbs-third generation initiator with good control over M_n and decent $Đ$ values. The resulting isoxazolidine-containing material could undergo further hydrogenation, deprotection, and modification with Dansyl chloride as well as ring opening to provide an amino-and hydroxyl-decorated "polyolefin."

1. Introduction

Ring opening metathesis polymerization (ROMP)[1] has become one of the preeminent methods of preparing designer macromolecules with controlled molecular weights, dispersities, and shapes that have found wide application throughout the scientific community.[2–6] Much of this is due to the living nature and the functional group tolerance of Grubbs-type initiators.[7] Because of their relatively simple preparations and high levels of ring strain, norbornene and oxanorbornene derivatives are the most commonly employed monomers for these reactions. Other strained cyclic compounds, like cyclobutenes,[8] have been polymerized as have medium-strained monomers (such as cyclooctene and cycloheptene derivatives[9,10]). Polymers derived from the latter three contain functionality directly connected to the polymer backbone, which can have dramatic effects on physical properties like glass transition (T_g) temperatures.[11] Additionally, as is the case for polymers made with acyclic diene metathesis[12] polymerization, these materials can undergo subsequent hydrogenation to provide functionalized, precision "polyethylenes."[13–18]

Similar materials can be prepared by polymerizing cyclopentene derivatives in which subsequent hydrogenation of the polypentenamer provides saturated, polyolefin analogues composed of precisely placed functionality.[19] The challenge behind this chemistry lies within the low levels of ring strain[10] and low ceiling temperatures (T_c) exhibited by such monomers. However, Neary and Kennemur have recently shown that polypentenamers can be prepared in high conversion with good control over molecular weight and $Đ$ using a variable-temperature approach.[20] The same lab (and others) have shown that polymers can be prepared with precisely placed functionality along the carbon backbone with mono-functionalized cyclopentenes.[11,21–26] However, preparing macromolecules from cyclopentenes functionalized at, both, the 1 and 3 positions seems to be less straightforward. Grubbs and co-workers showed the ROMP of 1,3-diol 1 (as well as its diester derivative 2) to be unsuccessful, due to the chelation to the metal center (**Figure 1**a).[27,28] Protecting the hydroxyl groups led to a temporarily strained monomer that could readily undergo ROMP (Figure 1b); subsequent deprotection and hydrogenation led to polyolefins containing precisely-placed hydroxyl groups.[28]

Inspired by these reports, we became curious as to whether or not it would be possible to incorporate dual functionalities into the polypentenamer architecture in a similar fashion to that summarized above. Coupled with this are curious examples from "small-molecule" synthetic chemistry that describe the use of the nitroso Diels–Alder (NDA) reaction as an efficient route toward substituted amino alcohols, compounds of importance to many fields (Figure 1c).[29–35] In particular, we were intrigued by the striking resemblance that some of these adducts share with norbornene, but were surprised to find that their polymerization by ROMP had yet to be explored. In fact, only a smattering of reports describing any olefin metathesis reactions for similar compounds exist, none of which involve metathesis polymerizations.[36–39]

Generally speaking, monomers constructed from virtually any hetero-Diels–Alder reaction have been studied to a much lesser extent than those prepared using "traditional" Diels–Alder chemistry. The few reports that do exist are almost exclusively focused on aza Diels–Alder reactions.[40–46] However, the utilization of nitroso Diels–Alder adducts as monomers for ROMP could allow for the preparation of some interesting, polar functional group-containing "polyolefins," materials of high interest to the polymer science community (Figure 1d).[47] This is especially interesting as it could possibly lead to polymers containing primary amines, materials that are challenging to prepare with ROMP.[48,49] At the very least, this can lead the way toward a simple synthetic route toward polyolefins decorated with both amino- and hydroxyl groups along the polymer backbone, materials that (as far as we can tell) have not yet been prepared via ROMP, but may have some potential biomedical applications.

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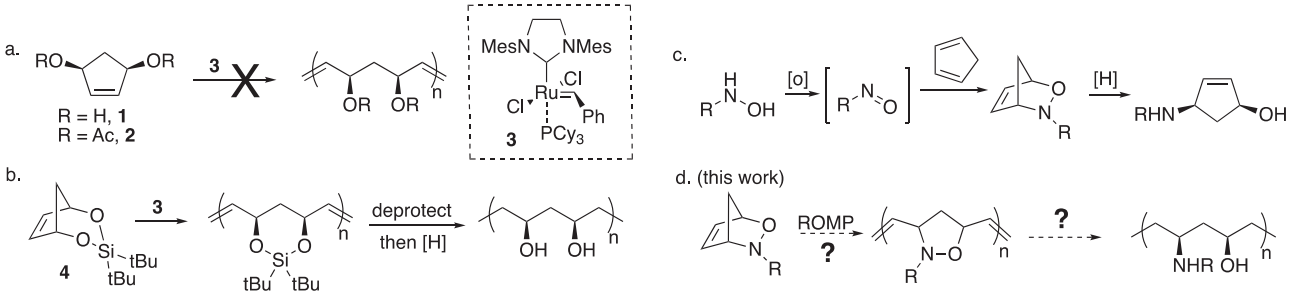
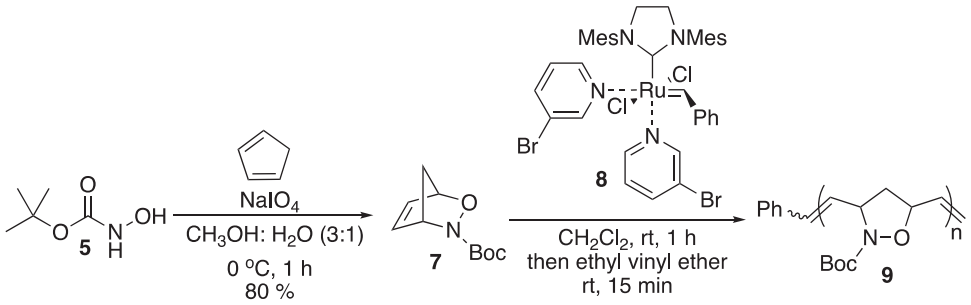


Figure 1. a) Attempted ROMP of monomers 1 and 2 by Grubbs second generation initiator 3 and b) ROMP of monomer 4 followed by deprotection and hydrogenation.[28] c) Depiction of general NDA reaction and reductive cleavage and d) the potential utility of this reaction for ROMP.



Scheme 1. Synthesis and ROMP of Diels–Alder adduct 7 to form polymer 9.

2. Results and Discussion

Our study commenced with the preparation of *N*-Boc-2-oxa-3-aza bicyclo[2.2.1]hept-5-ene (7) using adapted literature protocols.[50] This involved the reaction of *N*-Boc-hydroxylamine (5) with freshly cracked cyclopentadiene in the presence of sodium periodate in aqueous methanol (**Scheme 1**). 7 was isolated as an orange oil after flash column purification. Upon isolation of 7, its utility as a monomer for ROMP was investigated by subjecting it to reaction with Grubbs third generation initiator 8 ([M]:[I] = 65:1) in methylene chloride. After 1 h, ^{1}H NMR analysis showed 90% conversion. After quenching with ethyl vinyl ether and removal of excess solvent, polymer 9 was isolated as a gummy solid in 70% by trituration with cold (≈ −20 °C) ethyl ether. Confirmation of product formation was ascertained by ^{1}H NMR spectroscopy which revealed a disappearance of the singlet at 6.39 ppm (corresponding to the olefinic protons in 7) as well as the singlets at 5.19 and 4.97 ppm. These signals were replaced by broad signals at 5.91–5.40 ppm (corresponding to the olefinic backbone of 9) and broad signals at 5.08–4.84, 4.79–4.52, and 4.41–4.27 ppm (**Figure 2**). Analysis of 9 by ^{13}C NMR spectroscopy revealed little regio-or stereoselectivity, exhibiting multiple olefinic signals between 125 and 136 ppm (Supporting Information).

Gel permeation chromatography (GPC) analysis of 9 revealed relatively good control over M_n with a value of 29 000 Da, close to the theoretical value (M_n (theor)) of 28 845 Da (**Table 1**, entry 1). However, a broader than desired polydispersity index ($Đ$) of 1.33 was observed, but a linear increase of M_n values with increasing [M]:[I] ratio was found (**Figure 3**, Table 1). Unfortunately, we discovered that conversion dropped off steeply at higher [M]:[I] ratios (≥200:1), even with longer reaction times. Nevertheless, polymer 9 was found to be soluble in a wide

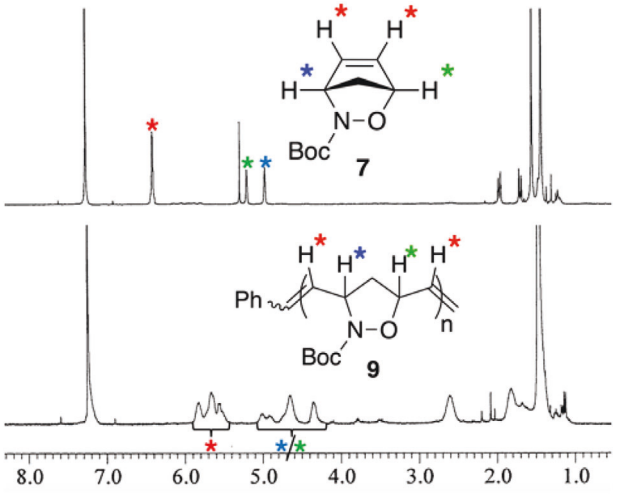


Figure 2. Partial ^{1}H NMR spectra of monomer 7 and polymer 9.

Table 1. Polymerizations of monomer 7 at various [M]:[I] ratios and analyses of resulting products.

Entry[a)]	[M]:[I]	M_n (theor)	M_n[b)]	$Đ$[b)]	Conv. [%][c)]
1	65:1	12 820	11 500	1.30	98
2	80:1	15 778	14 900	1.40	90
3	110:1	21 695	23 300	1.33	80
4	125:1	24 653	24 100	1.31	82
5	145:1	28 845	29 000	1.33	90

[a)] Polymerization conditions: [M] = 0.45 M in CH_2Cl_2, rt, 1 h; [b)] Determined by GPC; [c)] Determined by ^{1}H NMR spectroscopy.

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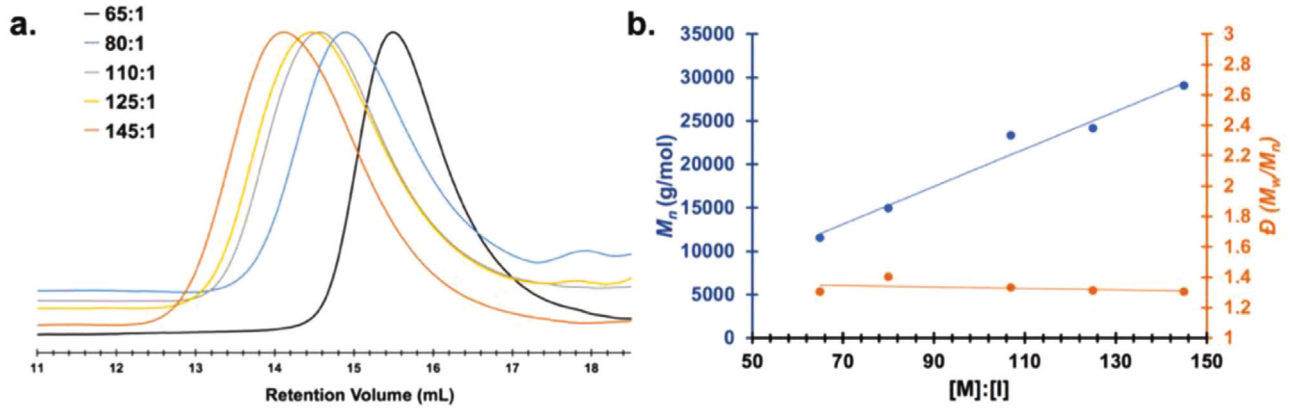
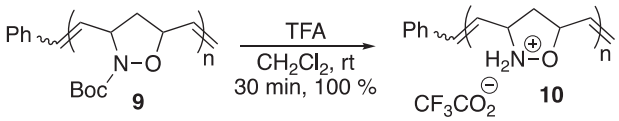


Figure 3. a) GPC traces of products from ROMP of monomer 7 at varying [M]:[I] ratios and b) change in M_n (blue) and $Đ$ (orange) as a function of [M]:[I].



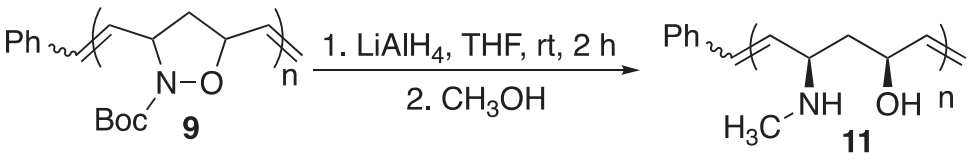
Scheme 2. TFA-mediated deprotection of 9.

range of organic solvents, including: methylene chloride, THF, acetone, methanol, ethanol, *N*-methyl-2-pyrrolidone (NMP), and *N,N*-dimethylformamide (DMF).

In order to render this macromolecular isoxazolidine amenable to further modification, it is critical to remove the Boc protecting group. So, we next attempted the trifluoroacetic acid (TFA)-mediated deprotection of 9 (**Scheme 2**). FT-IR analysis showed complete deprotection after 30 min through the disappearance of the signal at 1705 cm^{-1} (corresponding to the carbonyl stretch of the carbamate), the appearance of a sharp signal at 1683 cm^{-1} (corresponding to the trifluoroacetate carbonyl stretch) and a broad signal at 3400 cm^{-1} (indicative of NH stretches). By this point in the reaction, 10 had already precipitated and was isolated by removal of the excess solvent and TFA under reduced pressure. The resulting material was only partially soluble in methanol and exhibited no observable solubility in water or any other organic solvents, rendering its complete characterization and subsequent modification/functionalization futile. Changes in pH resulted in no noticeable difference in this solubility.

While not a traditional "deprotection," it has been documented that $LiAlH_4$ can mediate the transformation of Boc-carbamates into methyl amines, opening up the opportunity for modification at the N atom.[51] Additionally, $LiAlH_4$ has been shown to facilitate N–O reductive cleavage in isoxazolines and isoxazolidines.[52] So, we envisaged a one-pot strategy involving $LiAlH_4$-facilitated carbamate-to-amine transformation, followed by sequential reductive cleavage of 9's N–O bond (**Scheme 3**). This was accomplished by treating an anhydrous THF suspension of $LiAlH_4$ with a dropwise addition of a THF solution of 9. This led to the complete disappearance of the carbonyl stretch at 1705 cm^{-1} and was met with the appearance of broad signals between 3600 and 3100 cm^{-1} (indicative of NH and OH stretches) in the FT-IR spectrum. Quenching this reaction with excess methanol, followed by centrifugation allowed for the isolation of 11 (as a THF/methanol solution) by decantation. Removal of the solvent provided 11 as a light brown solid in 75% yield. Like 10, 11 exhibited extremely limited solubility. Curiously, it seemed to lack any solubility in any organic solvent on hand (even the solvents from which it was isolated, THF and methanol) at any practical temperature. We had originally thought that this was due to some unknown decomposition, resulting in an unexpected covalent crosslinking event. However, this may be a result of increasing intrachain hydrogen bonding interactions upon concentration, similar to previously studied materials.[53] A covalent crosslinking event was ruled out considering that 11 was completely soluble in dilute aqueous HCl (≈1 M). However, the acidic solution of polymer 11 became cloudy upon sitting (≈1 h) and eventually precipitated out of solution, pointing to possible side reactions under acidic conditions.

There are alternative routes to achieve isoxazolidine ring opening, several of which are more commonly employed than the $LiAlH_4$ facilitated chemistry used above.[35,52,54–57] One of the most widely used methods involves treatment of the isoxazolidine with $Mo(CO)_6$ and $NaBH_4$.[29] Alternatively, Ji and Miller[58] and others[59–62] have previously shown that catalytic hydrogenation can be an effective route toward N–O reductive cleavage.



Scheme 3. $LiAlH_4$-mediated, one-pot, carbamate-to-amine transformation/reductive cleavage of 9.

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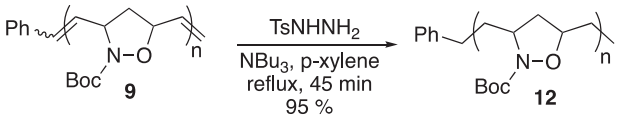
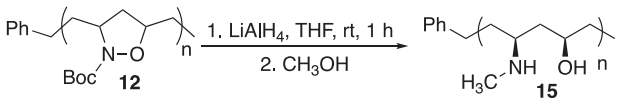


Scheme 4. Exhaustive hydrogenation of 9 with $TsNHNH_2$ to obtain saturated 12.



Scheme 6. $LiAlH_4$-mediated, one-pot, carbamate-to-amine transformation/reductive cleavage of 12 to form 15.

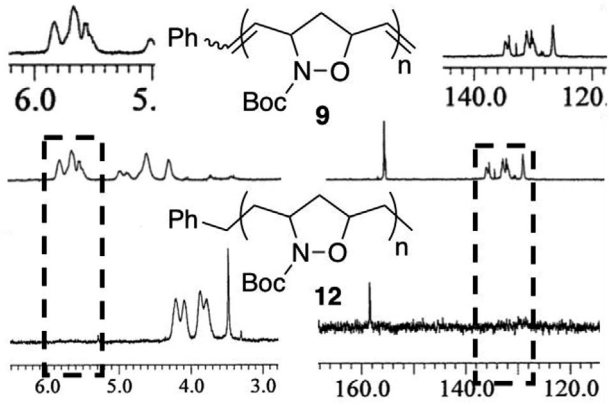
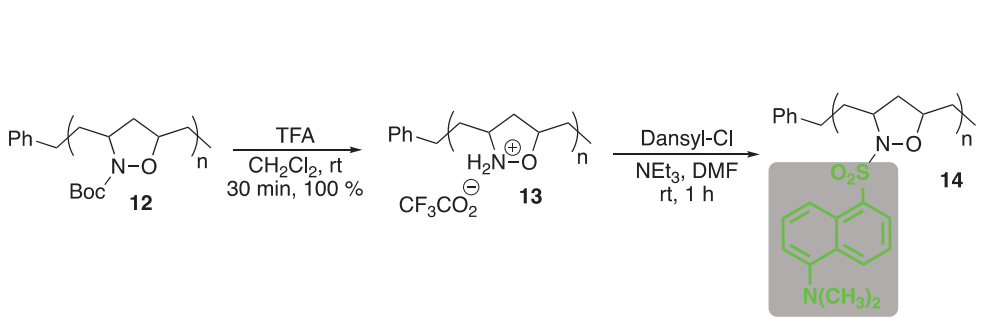


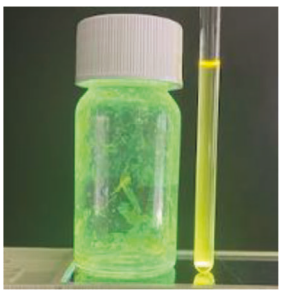
Figure 4. Partial ^1H (left) and ^{13}C (right) NMR spectra of unsaturated 9 (top) and saturated 12 (bottom) showing the disappearance of signals associated with olefinic environments.

Unfortunately for us, these methods led to intractable product mixtures or no observable reaction, respectively (Supporting Information).

As stated in the introduction, one of our ultimate goals was to utilize this chemistry as a potential route to amino-and hydroxyl-decorated "polyolefins." Generally, ROMP-derived polymers can easily be transformed into their saturated counterparts through exhaustive hydrogenation facilitated by *p*-toluenesulfonyl hydrazide ($TsNHNH_2$).[14] However, adapting such procedures for the reduction of 11 proved tricky, as it exhibits absolutely no solubility in hydrocarbon solvents. However, we did find that subjecting 9 (instead of 11) to reaction with $TsNHNH_2$ and tributylamine in refluxing *p*-xylene led to backbone hydrogenation in less than 1 h (**Scheme 4**). Product confirmation was ascertained by ^1H and ^{13}C NMR which revealed the nearly complete disappearance of the olefinic signals along the backbone of 9 (**Figure 4**). Advantageously, both ^1H and ^{13}C NMR spectra showed retention of the tenacious Boc protecting group (1.46 and 158.39 ppm, respectively). This was also confirmed in the FT-IR spectrum by the retention of the carbamate stretch. This analysis further revealed no hydroxyl or amino stretches, suggesting survival of the N–O bond, as well. Unfortunately, the exact extent of Boc retention was not able to be determined because reliable integration values in the ^1H NMR spectrum could be not obtained (in both 9 and 12) because of signal overlap in that region. Nevertheless, 12 was soluble in most organic solvents at our disposal including methylene chloride, chloroform, methanol, 80–90% aqueous methanol, ethanol, DMF, DMSO, and THF, making its purification by precipitation a bit challenging. It was found that 12 could be isolated as a brown solid through repeated triturations with cold (≈ −20 °C) diethyl ether, but its partial solubility had detrimental effects on isolated yields. Alternatively, 12 could be purified by flash chromatography (silica, 2:3 hexanes:ethyl acetate, then methylene chloride), but this (not unexpectedly) resulted in diminished yields and excess solvent waste. Alternatively, we found that this solid material could easily be purified and isolated as a white solid (in nearly quantitative yield) by trituration with copious amounts of water.

In order for this material to be amenable to further modification, we next set out to explore the TFA-mediated deprotection of 12. Indeed, this was as successful as it was for 9 earlier. Unfortunately, 12 exhibited a similar solubility profile to 9. But 12 was completely soluble in DMF, offering a glimmer of hope that some post-polymerization modifications at the N atom would be possible. As proof-of-concept, we found that treating a DMF solution of 12 with triethylamine and Dansyl chloride led to the formation of 14 as light yellow and brilliantly fluorescent solid after precipitation into methanol (**Scheme 5**). Dansyl chloride was chosen since its fluorescence would serve as a qualitative indication of successful deprotection in the event that solubility issues hamper NMR analysis. Although 14's solubility was limited, it did show very slight solubility in DMSO, allowing for characterization by NMR which revealed the appearance of signals between 8.5–7.0 ppm (corresponding to the Dansyl-aromatic protons).





Scheme 5. Boc deprotection of 12 followed by reaction with Dansyl chloride and photograph showing the fluorescence of 14 as a solid and solution (in DMSO-d_6).

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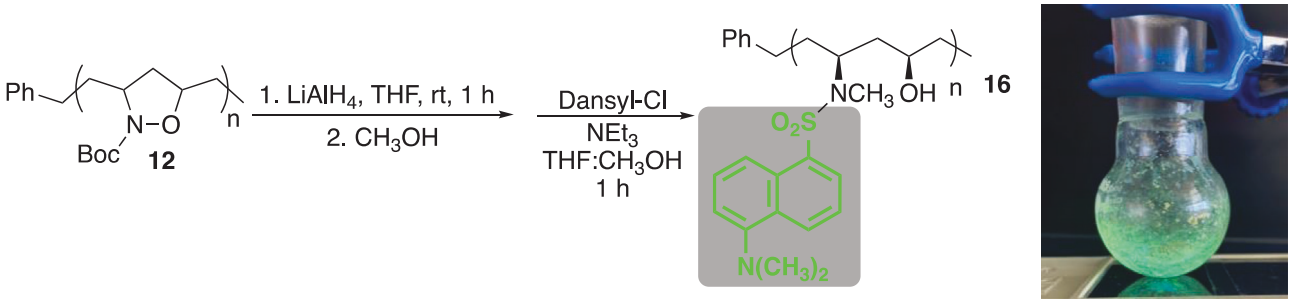

Scheme 7. $LiAlH_4$-mediated, one-pot, carbamate-to-amine transformation/reductive cleavage of 12 and its post-polymerization modification with Dansyl chloride and photograph showing the fluorescence of 16.

We next decided to explore the efficacy of the same $LiAlH_4$-mediated, one-pot transformation described above in Scheme 4. Indeed, the same procedure utilized for 9 led to complete carbamate transformation and ring opening of 12 to form 15 (**Scheme 6**), as indicated by FT-IR spectroscopy. Although completely soluble throughout the reaction and isolation, the resulting material 13 seemed to have lost all solubility upon concentration; addition of any solvent (even THF) failed to affect its dissolution (even upon gentle heating), similar to that observed for polymer 11. Additionally, the possibility of any covalent crosslinking was ruled out due to the complete solubility this material exhibited in dilute, aqueous HCl (≈1 M). Addition of K_2CO_3 to this solution triggered the precipitation of 15, a process that is seemingly repeatable in perpetuity.

Regardless of 15's relentless insolubility, it was possible to carry out further modifications without its actual isolation. This was accomplished by directly subjecting the methanolic-THF solution of 15 (isolated after centrifugation) to reaction with NEt_3 and Dansyl chloride (**Scheme 7**). After 1 h, 16 was isolated as a light yellow and highly fluorescent solid in 65% yield by trituration with copious amounts of water followed by methanol. FT-IR analysis revealed the complete absence of any carbonyl stretch and the appearance of a broad O-H stretch at ≈3390 cm^{-1} (Supporting Information). Unfortunately, once isolated, 16 exhibited the same solubility issues that were observed for 15, so no further characterization could be obtained. However, this material formed a solution in acidic water, in turn, quenching the fluorescence. Addition of K_2CO_3 triggered the precipitation of 16 as an off-white, fluorescent, waxy solid.

3. Conclusions

In conclusion, we have found that a simple, nitroso Diels–Alder reaction leads to a strained ring that can undergo facile polymerization in the presence of Grubbs-third generation initiator. The polymerizations occur with good control over M_n and acceptable $Đ$ values. Attempts at any post-polymerization deprotection or ring opening led to material that was only sparingly soluble. Though, exhaustive hydrogenation led to a new, saturated isoxazolidine-containing material that could undergo further modifications (i.e., deprotection, ring opening, etc.) to provide fluorescently labelled polymers as well as amino-and hydroxyl-decorated "polyolefins" that exhibit reversible water-solubility behavior in response to changes in pH. Unfortunately, many of these materials were plagued by extremely limited solubilities; methods aimed at increasing their solubilities (and, in turn, their processabilities) by expanding monomer scope as well as the preparation of copolymers are currently being investigated.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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