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High Molecular Weight Semicrystalline Substituted Polycyclohexene From Alternating Copolymerization of Butadiene and Methacrylate and Its Ambient Depolymerization

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Cite This: J. Am. Chem. Soc. 2024, 146, 25321−25327
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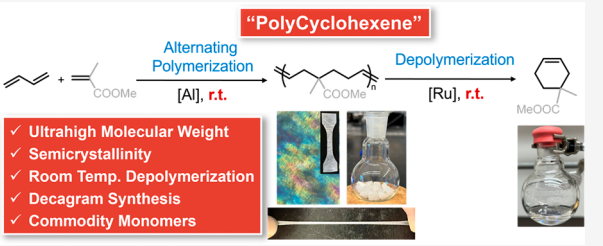
ABSTRACT: Cyclohexene cannot be polymerized via ring-opening polymerization under any conditions due to its lack of ring strain. A hypothetical polycyclohexene would therefore have a strong thermodynamic driving force to depolymerize to monomer if a metathesis catalyst were provided while otherwise having thermal and hydrolytic stability under normal conditions because of its hydrocarbon backbone. We envisioned access to this otherwise unattainable family of polymers via the alternating polymerization of a diene and an alkene. Ethyl aluminum chloride was found to promote highly alternating polymerization of butadiene and methacrylate when radically initiated at room temperature, resulting in formal polycyclohexene structures. Ultrahigh molecular weight (up to 1750 kDa) polymers can be synthesized at the decagram scale in high monomer conversions. The resulting presumably atactic copolymers exhibited semicrystallinity, leading to high toughness. In the presence of a small amount of the Grubbs catalyst, the generated polycyclohexene can be fully depolymerized at ambient temperatures into pure constituent cyclohexene. The strategy of using orthogonal chemistry for the polymerization and depolymerization processes allows access to polymer structures with subambient ceiling temperatures without using ultralow temperature synthesis or relying on the monomer-polymer equilibrium.



INTRODUCTION

Depolymerizable polymers have received extensive interest for addressing the environmental challenges of plastics and enabling novel materials.[1−4] Most polymerization processes are exothermic and exoentropic ($\Delta H < 0$, $\Delta S < 0$). The temperature at which the entropic loss offsets the enthalpic gain is defined as the polymer ceiling temperature (T_c) and depolymerization becomes favored when the temperature is above T_c.[5] Ideally, depolymerizable polymers would (1) have low T_c's to allow facile depolymerization, but at the same time be thermally stable; (2) present a high kinetic barrier to prevent depolymerization or degradation under normal usage and environmental conditions, so that the depolymerization can only be triggered on demand; (3) be synthetically accessible using readily available monomers at a large scale; (4) generate only clean and nontoxic products upon depolymerization. Classic low T_c polymers, such as poly(olefin sulfones)[6] and poly(*o*-phthalaldehydes),[7,8] require very low temperatures for their syntheses, lack thermal and chemical stability, and generate toxic molecules when depolymerized. Most recent designs of depolymerizable systems are based on ring-opening polymerizations with elegant manipulation of strain and conformation of cyclic monomers to favor polymerization or depolymerization at different temperatures and monomer concentrations.[2,3,5,9−18] For example, new designs of mono or bicyclic lactones,[10−14] thiolactones,[15,16] and cyclic acetals[17,18] allowed their reversible polymerization and depolymerization at moderate temperatures. Depolymerizable systems from radical chemistry are much less common and typically have a high T_c. Polymethacrylates synthesized by reversible-deactivation radical polymerizations represent a notable recent example with practically accessible depolymerization temperatures.[19−22] It still remains challenging to achieve depolymerization at ambient temperatures and obtain depolymerizable polymers with ultrahigh MWs, because of the delicate thermodynamic balance for the equilibrium between polymerization and depolymerization.

We envisioned bypassing monomer-polymer equilibrium through a different approach: using orthogonal chemistry for polymerization and depolymerization of the same polymer structure.

Olefin metathesis is attractive catalytic chemistry for depolymerization[23,24] since metathesis reactions using robust and highly active Grubbs catalysts are mild, efficient, and tolerant to a variety of functional groups. Metathesis-based

Received: July 18, 2024
Revised: August 23, 2024
Accepted: August 23, 2024
Published: September 2, 2024

depolymerizable polymers typically consist of hydrocarbon backbones, which ensure thermal and hydrolytic stability during their lifetime but can be depolymerized at their end-of-life when a catalyst is introduced or activated.

Cyclopentene-based monomers have long been explored for olefin metathesis depolymerization,[25−28] due to their relatively low ring strain, but their low strain can also limit achievable conversion and molecular weights, especially for substituted cyclopentenes. Recently, Wang and co-workers cleverly designed a series of *trans*-ring fused cyclooctenes that can be reversibly polymerized and depolymerized.[29−32] However, the specialty monomers require multistep synthesis, which may limit their practical applications. Additionally, both the polymerization and depolymerization of these metathesis depolymerizable polymers are based on olefin metathesis chemistry, doubling the catalyst usage and requiring variation in reaction conditions (concentration and temperature) to favor the equilibrium toward polymerization or depolymerization.

Cyclohexene is strainless and essentially unpolymerizable via ring-opening polymerization under any conditions, as shown experimentally[33] and computationally.[34] McCarthy and co-workers reported that only short oligomers with 2−6 repeat units were formed even at −116 °C.[33] Thus, once an active metathesis catalyst is introduced, polycyclohexene would have an extremely strong thermodynamic driving force to completely depolymerize into cyclohexene, even at bulk monomer concentrations. On the other hand, the extremely unfavorable thermodynamics of the ring-opening polymerization of cyclohexene prevents the direct synthesis of polycyclohexene via olefin metathesis. We imagined overcoming these thermodynamic limitations intrinsic to ring opening polymerization of cyclohexene by synthesizing a polymer with the same backbone structure through an orthogonal approach: alternating copolymerization of a diene (via 1,4-addition) and a terminal alkene (Figure 1).

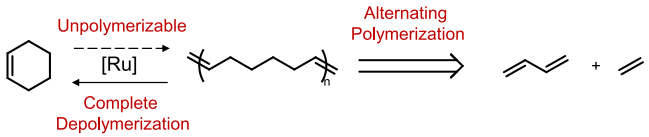


Figure 1. Formally polycyclohexene can be generated through alternating copolymerization between a diene and an alkene and depolymerized via olefin metathesis.

Herein, we report the synthesis of formal polycyclohexene from the alternating copolymerization of butadiene and methacrylate, both commodity chemicals. Ultrahigh molecular weight, perfectly alternating copolymers can be obtained in high yields at the multigram scale. We also demonstrated the complete depolymerization of the resulting polycyclohexene to pure cyclohexene in the presence of a Grubbs catalyst.

RESULTS AND DISCUSSION

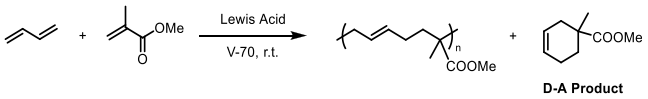
Lewis acids are known to promote alternating radical copolymerization of alkenes with different electronics and reactivity ((meth)acrylate-*co*-1-alkene,[35−37] styrene-*co*-methacrylate,[38,39] or vinyl ether-*co*-acrylate[40]). Of particular interest to us was the alternating copolymerization of a diene and an alkene. In the 1970s, Furukawa and co-workers studied the copolymerization of conjugated dienes with acrylonitrile (AN) or methyl methacrylate (MMA) using $EtAlCl_2$−$VOCl_3$ as the catalyst.[41,42] The polymerization was redox-initiated and showed a strong tendency for comonomer alternation, while the detailed mechanism was not resolved. Insoluble gelation typically occurred unless the copolymerization was carefully monitored to stop at low conversions, limiting the polymer yield.[41,42] Ban et al. reported that methylaluminoxane (MAO) can effectively initiate and promote alternating polymerization of butadiene (BD) with MMA, but the polymer yield was low (<20%) and the dispersity was rather high (around 4).[43]

We decided to explore the free radical copolymerization of BD and MMA in the presence of a Lewis acid because their successful alternating copolymerization would yield a formal polycyclohexene backbone. Our initial attempts at running the copolymerization of BD and MMA at 60 °C using AIBN as the initiator in the presence of Et_2AlCl as a Lewis acid resulted in only negligible polymer formation, but 62% conversion to the Diels−Alder (DA) product between the two monomers. To minimize the DA reaction, we attempted the copolymerization at room temperature using V-70 as the initiator.[44] We first carried out the copolymerization at equal loading of BD and MMA at 2 M each in toluene with 0.2 equiv of a Lewis acid relative to MMA. $ZnCl_2$ did not give any conversion, and $AlCl_3$ only resulted in moderate conversion to the DA product after 5 h. Without a Lewis acid, V-70 and monomers alone also did not give any product at room temperature. In contrast, the presence of Et_2AlCl gave 44% monomer conversion to copolymer and <2% to the DA product after 5 h. Gratifyingly, using more acidic $Et_{1.5}AlCl_{1.5}$ resulted in >85% conversion to copolymer with <4% DA product within 5 h (entries 1−4, Table 1). Further, both BD and MMA were consumed at the same rate (Figure S1). The ^1H and ^{13}C NMR spectra of the resulting copolymers suggested very high degrees of alternation (Figure 2). The alkene proton region showed two sets of clean doublet and triplet signals at 5.32 and 5.21 ppm, corresponding to H_b and H_c, respectively (Figures 2a and S2). Further, the doublet coupling constant was calculated to be 15 Hz, indicating predominantly a *trans* configuration for the backbone alkenes. A very weak signal of terminal alkene at 4.80 ppm was visible, corresponding to 1,2-addition of BD, but it only accounts for <4% of the BD units (Figure 2a). The other signals in the aliphatic region clearly correlated to each backbone proton (H_a, H_d, and H_e) expected from the alternating structure. The ^{13}C NMR spectrum showed two predominant alkene signals, supporting one configuration for the backbone alkenes, and all other signals agree with the assignment of the alternating structure (Figure 2b). Only one ^{13}C NMR signal was observed for the backbone chiral carbon, but this cannot determine the tacticity of the resulting polymer due to the long distance between the chiral centers along the backbone. Even when the comonomer loading is unequal (BD:MMA = 3:2 or 2:3) (entries 5−6, Table 1), high fidelity in the alternating sequence was maintained without noticeable formation of homodiads, as revealed by NMR spectroscopy (Figure S3). We then chose $Et_{1.5}AlCl_{1.5}$ as the Lewis acid for further investigation due to its relatively fast polymerization.

NMR spectroscopy revealed the complexation of the Lewis acid with the monomer and resulting polymer. Upon the addition of $Et_{1.5}AlCl_{1.5}$ to the mixture of MMA and BD, the alkene and methyl proton signals arising from MMA have all shifted downfield compared to those of noncomplexed MMA, while the signals from BD remained unchanged (Figure 3). This observation indicated that rapid equilibrium between free

https://doi.org/10.1021/jacs.4c09811
J. Am. Chem. Soc. 2024, 146, 25321−25327

Table 1. Optimization of the Alternating Copolymerization Conditions[a]



entry	BD:MMA:LA:V-70	LA	reaction time (h)	polymer yield[b]	D-A product yield[b]	$M_{n,SEC}$ (kDa)[c]	$\mathit{110}$[c]
1	20:20:4:1	$AlCl_3$	5	4%	33%	N/A	N/A
2	20:20:4:1	$ZnCl_2$	5	0%	0%	N/A	N/A
3	20:20:4:1	Et_2AlCl	5	44%	1.5%	32.6	1.26
4	20:20:4:1	$Et_{1.5}AlCl_{1.5}$	5	85%	3.6%	43.4	1.45
5	30:20:4:1	$Et_{1.5}AlCl_{1.5}$	5	82%	3.8%	44.2	1.73
6	20:30:4:1	$Et_{1.5}AlCl_{1.5}$	5	83%	2.3%	58.0	1.33
7	20:20:8:1	$Et_{1.5}AlCl_{1.5}$	5	95%	2.3%	59.3	1.46
8	20:20:16:1	$Et_{1.5}AlCl_{1.5}$	1.5	98%	2.5%	104	1.67
9	20:20:4:0.2	$Et_{1.5}AlCl_{1.5}$	5	50%	6%	145	1.45
10	20:20:8:0.1	$Et_{1.5}AlCl_{1.5}$	12	88%	6%	197	1.36
11	20:20:8:0.05	$Et_{1.5}AlCl_{1.5}$	12	84%	7%	400	1.29
12	20:20:8:0.01	$Et_{1.5}AlCl_{1.5}$	12	85%	10%	1180	1.43
13[d]	20:20:8:0.005	$Et_{1.5}AlCl_{1.5}$	24	85%	14%	1750	1.50[e]

[a]The reaction was performed under N_2 in a Schlenk tube at room temperature at 4 mmol scale. [b]Determined by ^{1}H NMR spectroscopy. [c]Determined by SEC MALLS analysis in THF. [d]Polymerization was carried out at 150 mmol scale, 16 g MMA and 75.2 mL 1,3-butadiene(15 wt % in toluene) are used. [e]Likely underestimated as the molecular weight approaches the column separation limit.

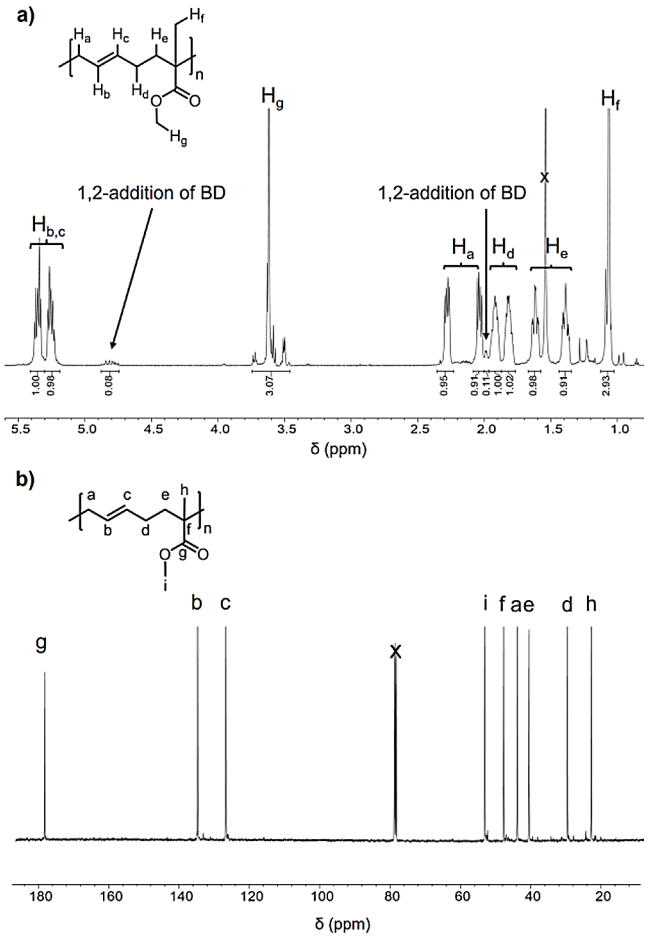


Figure 2. Partial ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of synthesized poly(BD-*alt*-MMA).

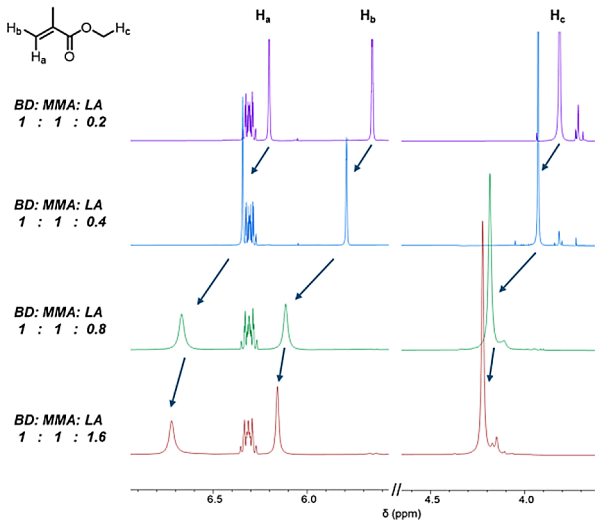


Figure 3. Stacked partial ^{1}H NMR (400 MHz, $CDCl_3$) spectra of the BD and MMA mixture with different $Et_{1.5}AlCl_{1.5}$ loadings.

and complex MMA results in a merged signal at the NMR time scale, and BD is not involved in the complexation to preform a ternary complex as suggested in the previous literature.[42] The high degree of alternation is likely regulated by the strongly favored cross-propagation due to the enhanced difference in monomer polarity in the presence of the Lewis acid.[45] As $Et_{1.5}AlCl_{1.5}$ stoichiometry was increased from 0.2 to 1.6 eq relative to MMA, the alkene and methoxy proton signals of MMA progressively shifted downfield, shifting 0.47 and 0.43 ppm, respectively. Using Job plot analysis at a 2 M total concentration of MMA and $Et_{1.5}AlCl_{1.5}$ (Figure S4), we calculated the averaged stoichiometry of complex X_{max} to be 0.5, which indicates a 1:1 coordination between MMA and aluminum species. We also observed that the complexation of Lewis acid with MMA is competitively stronger than with the resulting polymer (Figure S5).

We further investigated the effect of varying the stoichiometry of $Et_{1.5}AlCl_{1.5}$ on the copolymerization. Increasing $Et_{1.5}AlCl_{1.5}$ loading resulted in faster copolymerization, reaching 95% conversion after 5 and 1.5 h for $Et_{1.5}AlCl_{1.5}$ loading at 0.4 and 0.8 eq relative to MMA, respectively. M_n of the resulting polymers also progressively increased from 43 to

https://doi.org/10.1021/jacs.4c09811
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101 kDa with increasing LA loading, measured by size exclusion chromatography (SEC) with multiangle laser light scattering (MALLS) detection (entry 4, 7, and 8, Table 1, Figure S6). This observation may suggest faster monomer addition to the growing chain ends before termination occurs as the LA loading increases. The molar mass distribution of all the resulting polymers was monomodal with dispersities around 1.4−1.7. All the LA loadings gave equally highly alternating polymers and minimal formation of DA product (<4%).

Lastly, we varied the radical initiator loading. As V-70 was decreased to below 1 mol % relative to MMA or BD, the copolymerization slowed down but can be promoted by increasing the LA loading from 0.2 to 0.4 equiv (entries 9−13, Table 1). At low initiator loadings, gelation of the solution occurred within 2 h, and we allowed the polymerization to proceed for 24 h. M_n's of the produced polymers monotonically increased from 197 to 400 to 1180 kDa when the initiator loading was reduced from 0.5 to 0.25 to 0.05 mol % (Figure 4a,

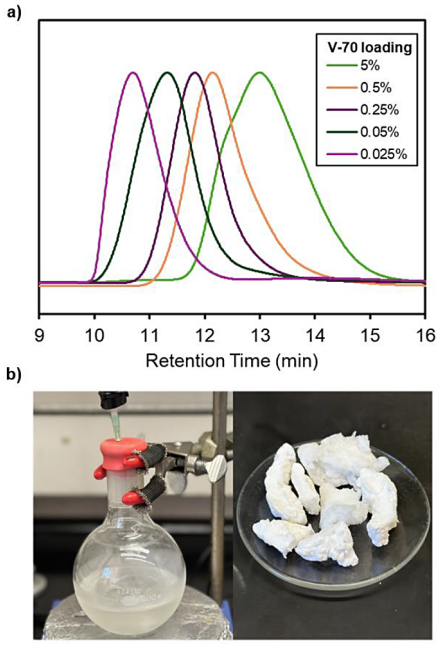

Figure 4. (a) SEC chromatograms of synthesized poly(BD-*alt*-MMA) at different initiator loadings (5−0.025% V-70, entry 7, 10−13, Table 1), (b) photos of 24 g scale polymerization and 19 g of isolated poly(BD-*alt*-MMA).

entry 10−12, Table 1). Remarkably, ultrahigh molecular weight (M_n > 1.7 MDa) polymers were obtained at 85% conversion and decagram scale using 0.025 mol % V-70 (Figure 4b, entry 13, Table 1). Additionally, good reproducibility of yield, molecular weight, and perfect alternation was obtained under these polymerization conditions and at different scales (Table S1). The significant improvement in the yield and molecular weight of alternating copolymers over previous reports mainly stems from using a radical initiator and running the polymerization at room temperature. Mechanistic details of this copolymerization system warrant further investigation.

Interestingly, the solution-cast or melt-pressed poly(BD-*alt*-MMA) samples turned opaque at room temperature and showed strong birefringence under a polarized light microscope (Figure 5a), suggesting semicrystallinity despite the assumed atactic backbone microstructure. Differential scanning

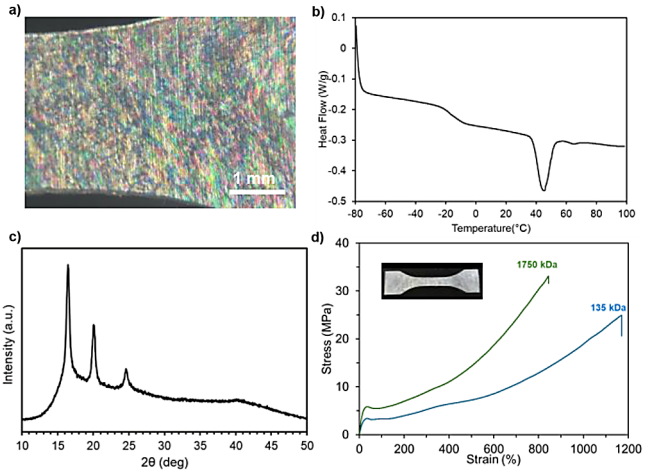

Figure 5. Analysis of melt pressed p(BD-*alt*-MMA) using (a) polarized light microscope, (b) DSC, (c) PXRD, and (d) tensile test.

calorimetry (DSC) showed a T_m of 45 °C in addition to a T_g at −16 °C (Figure 5b). Powder X-ray diffraction (PXRD) of the samples gave crystalline diffraction signals at 2θ = 16.5°, 20.0°, and 24.6°, further confirming the semicrystallinity (Figure 5c). While atactic polymers can exhibit semicrystallinity, such polymers remain uncommon.[16,46−50] Dogbone samples of poly(BD-*alt*-MMA) with M_n = 135 and 1750 kDa were prepared and subjected to uniaxial tensile testing. Both samples exhibited notable strain stiffening upon elongation, reaching an ultimate tensile strength of 33 MPa at 840% strain at break for the 1750 kDa polymer and 26 MPa at 1170% strain at break for the 135 kDa polymer (Figure 5d). The strain stiffening gave a high toughness of about 120 MJ/m^3 for both polymers.

We next investigated the depolymerization of the synthesized "polycyclohexene" via olefin metathesis using Grubbs catalysts at room temperature (Tables S2 and S3), considering the strongly favorable thermodynamics for its depolymerization. In the presence of 0.5 mol % Grubbs II or Hoveyda-Grubbs II catalyst, complete depolymerization in 25 wt % polymer solution proceeded cleanly to the expected 1,1-methyl methylcarboxylate cyclohexene within 2 h. SEC analysis of the depolymerization mixture showed a gradual reduction of the overall molecular weights over time, suggesting that the depolymerization is via a random chain cleavage process (Figure 6a). Lowering the catalyst loading to 0.3 mol % slowed the depolymerization, but complete depolymerization was still achieved in 24 h at room temperature. While further lowering the catalyst loading to 0.1 mol % gave ∼85% depolymerization after 24 h, slightly warming the solution to 40 °C resulted in complete depolymerization. We next attempted depolymerization of the bulk polymer. Thermodynamically, polycyclohexene should undergo metathesis depolymerization in bulk, but simply mixing solid catalysts with solid polymers did not trigger depolymerization due to the poor dispersion and dissolution of catalysts in the polymer. Thus, a small amount of solvent was used to first dissolve the catalyst and then added to the solid polymer. Nearly complete depolymerization was observed in 24−48 h using 0.5 mol % catalyst. We further demonstrated a 5 g scale depolymerization using 0.3 mol % Grubbs II catalyst in THF solution. After the depolymerization

https://doi.org/10.1021/jacs.4c09811
J. Am. Chem. Soc. 2024, 146, 25321−25327

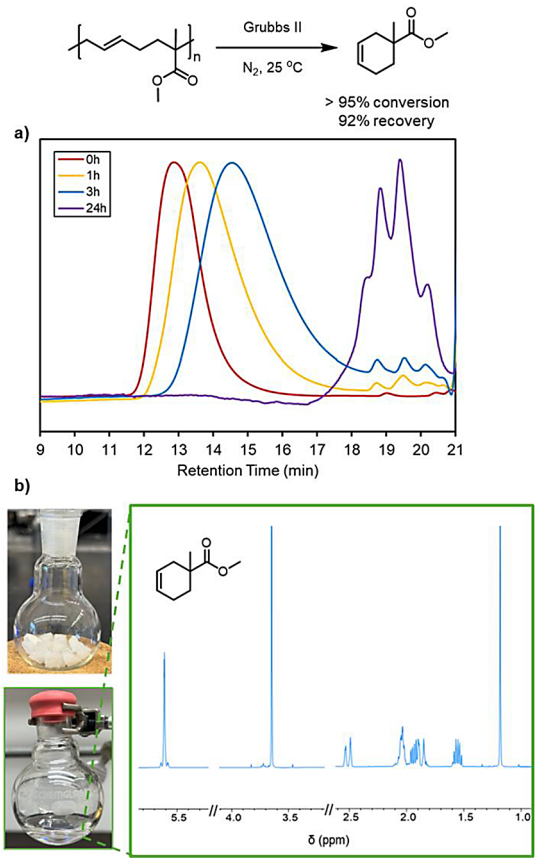

Figure 6. Ambient metathesis depolymerization of formally polycyclohexene. (a) SEC monitoring of the molecular weight change during depolymerization; (b) 5 g scale depolymerization with photos of 5 g of polymer (top left) and 4.6 g of isolated cyclohexene product and its ^{1}H NMR (400 MHz, $CDCl_3$) spectrum.

was allowed to proceed for 24 h at room temperature, a simple distillation recovered 4.6 g of pure 1-carbomethoxy-1-methylcyclohex-3-ene as a colorless fragrant liquid (92% isolated yield, Figure 6b), which is a high-value chemical and may be upcycled in other chemical processes.

CONCLUSIONS

We describe the synthesis of formal polycyclohexene via alternating copolymerization of butadiene and methacrylate. Using aluminum-based Lewis acid and performing polymerization at room temperature is key to obtaining high molecular weight polymers with highly alternating sequences and high monomer conversions. The resulting polymers exhibited semicrystallinity, despite presumably atactic microstructures and high toughness. The resulting polymers can fully depolymerize into substituted cyclohexene at room temperature by using a Grubbs catalyst. The use of commodity monomers, scalable synthesis, and accessible ultrahigh molecular weights make these polymers attractive as depolymerizable or immolative materials. The use of orthogonal chemistries for polymerization and depolymerization allows access to a class of thermally and hydrolytically stable polymers with very low T_c, which can undergo on-demand depolymerization at room temperature when a metathesis catalyst is introduced. We will further explore the scope of this highly alternating and efficient copolymerization to access depolymerizable polymers with tunable thermomechanical properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c09811.

Detailed experimental procedures and characterizations, additional ^{1}H and ^{13}C NMR spectra and GPC traces (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (CHE-2106511). We thank Ruilin Yin for help with thermal and mechanical measurements and Clara Zwanziger for help with XRD measurements. Part of this work was performed at the Stanford Nano Shared Facilities (SNSF), supported by the National Science Foundation under award ECCS-2026822.

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https://doi.org/10.1021/jacs.4c09811
J. Am. Chem. Soc. 2024, 146, 25321−25327