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Recyclable Biomass-Derived Polyethylene-like Plastics

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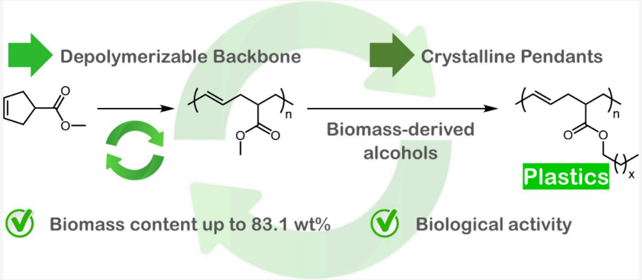

ABSTRACT: Recyclability and reusability of polymeric materials to reduce plastic wastes and alleviate environmental burdens have received extensive attention. Cyclic olefins with low ring strain and their depolymerizable polymers are very promising candidates. Introducing a linear alkyl side chain with a strong crystallization tendency to the backbone can endow the developed cyclopentene-based polypentenamers with comparable tensile properties to polyethylene. Nevertheless, the emerging challenge is their potentially high manufacturing cost and low sustainability, since stoichiometric petrochemical feedstocks need to be employed. To address the chemistry issues, we probe herein the protocol to prepare biomass-derived polypentenamers. Cyclopentene derivative methyl 3-cyclopentenecarboxylate was used to form a depolymerizable polymeric backbone and to create a powerful platform for synthesis of crystalline polypentenamers. Three biomass alcohols including biologically active natural product melissyl alcohol would act as the crystalline modules to be introduced into the polymers by transesterification using very few base catalysts. These depolymerizable plastics with a biomass content up to 83.1 wt % showed enhanced mechanical properties and could perform as mulch films to promote the growth of leafy crops. Complete depolymerization of these polymers to afford polymerizable monomers realized full closed-loop recycling. Diverse postfunctionalization to form versatile substances confirmed their reusability.

■ INTRODUCTION

In recent years, upcycling of polymer materials has attracted increasing interest. To alleviate environmental problems caused by disposal of plastic wastes, recyclability and reuse of polymers have become increasingly necessary.[1−3] Without compromising their inherent mechanical properties, however, endowing polymers with capability of depolymerization or degradation is formidably challenging.[4−7] During that process, bringing the polymer other new favorable functional properties concurrently becomes another fantastic topic. Presently, there are several protocols that are able to well recover the polymer wastes.[8−11] The very initial inner driven force is the cleavability or reversibility of units introduced into the polymer backbone.[12−38] For instance, by introducing C═C double bonds,[12−22] esters,[23−30] ketones,[31−34] and so forth into the main chain, people can employ olefin−olefin metathesis reaction with small olefins like ethylene to break the backbone into short segments, or hydrolysis to cleave the esters, or UV light to fragment the ketones. Based on this protocol, some chemically stable polymers, e.g., polyolefins, can be degraded into reusable even polymerizable molecules. Another strategy is to polymerize monomers with low ceiling temperatures of polymerization into polymers and then to depolymerize them in a mild condition after use. This full carbon closed-loop recycling protocol is practically sustainable and has been realized using many cyclic monomers, e.g., tetrahydrofuran,[39] 1,3-dioxolane,[40] 2,3-dihydrofuran,[41−44] cycloolefins, and their derivatives.[45−48] The common attribute of these monomers is their low ring strains. For instance, tetrahydrofuran has a ring strain of less than 9.6 kcal/mol while cyclopentene and its derivatives showed lower ring strains below 8 kcal/mol.[49] The well-controlled equilibrium (de)polymerizability can be established using temperatures according to the ring strain of the monomers.

Chemical recycling strategies described above are becoming a research topic in academia and industry. Recovering carbon resources or energy in the polymeric wastes will enable to resolve economic issues, environmental problems, and social burdens.[50−57] For polymeric materials, we usually employ them for some single-purpose use rather than for multipurpose applications. As a consequence, it is inevitable that more materials are employed to achieve the ultimate target. This has been a particularly noteworthy issue in agriculture for a long time. For example, mulch films made from low-density polyethylene (LDPE) are used to solely keep the warm and humid atmosphere for crops. Because they are not able to release useful chemicals like pesticides or growth regulators,

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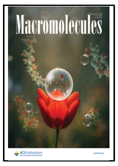

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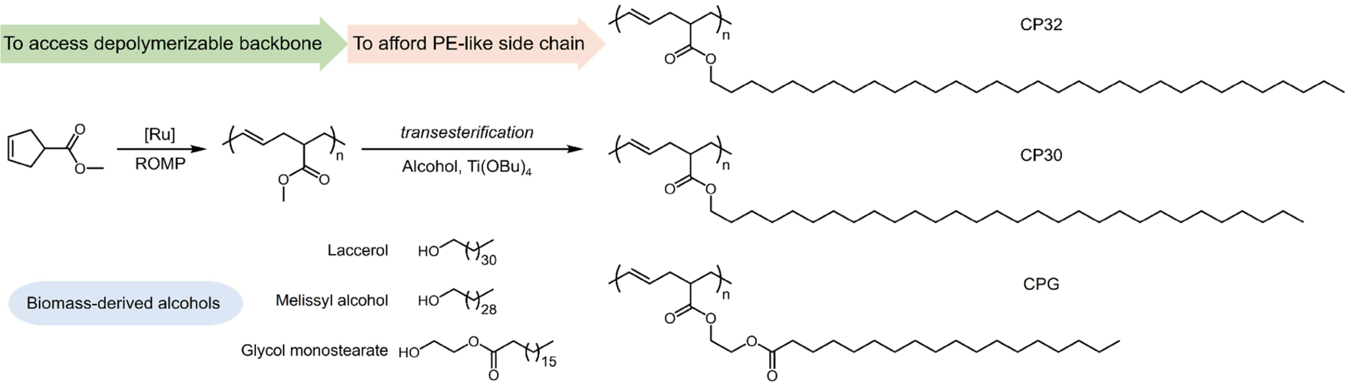
Scheme 1. Synthesis of Polypentenamer Materials by Petrochemical Cyclopentene-Based Monomer to Access the Depolymerizable Backbone and by Biomass-Derived Alcohols to Afford PE-Like Crystalline Side Chains



people have to spray these agents by ripping mulch films, which, however, do not exert the pesticide efficacy fully and timely. Their further applications are underexplored. On the other hand, for polymer chemistry, more properties than expected are always welcome to be introduced into newly developed single polymer material. That would greatly lower manufacturing cost and save feedstocks.[58,59] From these perspectives, it is preferred to bring the polymer new favorable properties concurrently, except for the aforementioned depolymerizability or degradability. For instance, it would be useful to introduce some components with biological activity into LDPE-like mulch film materials. Since it always brings worries concerning these plastic wastes after use as it often takes it for granted that they firmly would have detrimental impacts on plants or other creatures instead of any positive outcome,[1−4,50,51] these bioactive chemicals should promote growth of crops or inhibit insect pests or perform other environmental benign. In addition, they should show few negative effects on the material's performance of initial purpose. Instead, enhancement of the mechanical properties and lowering of the manufacturing cost are favorably expected.

We very recently reported a series of recyclable polypentenamers that contained different alkyl side chains ranging from nonyl to octacosyl.[48] Their polycyclopentene backbone promoted highly efficient degradation into their original building blocks (cyclopentene-derivative monomers), which can be repolymerized to form polymers, thus realizing a full closed-loop circular economy. The long linear crystalline alkyl chains would enable the polymers to form lamellae with precisely defined thicknesses of sub-5 nm. These degradable polycyclopentene-backboned polymers with crystalline pendants hold promise as commodity plastics. However, the laborious and tedious synthesis of monomers using many stoichiometric coupling reagents would increase the cost of large-scale manufacture and raise barriers to be industrial commodities. Therefore, we would like to make continuous endeavors to the chemistry issue. Herein, we contributed a study on a new protocol to access this kind of sustainable polymeric materials. They were derived from biomass feedstocks and showed mechanical properties comparable to the widely used LDPE. The major novelties are as follows: (i) The degradation polymer backbone was designed using a polypentenamer main chain, of which the polycyclopentene module can be depolymerized efficiently under mild conditions by very few catalysts. Degraded monomers can be reused to prepare the original methyl 3-cyclopentenecarboxylate or other uncommercially available alkyl 3-cyclopentenecarboxylates. Both of them will be polymerized to afford recyclable polymers, realizing full closed-loop recycling. (ii) Three biomass alcohols (laccerol, melissyl alcohol, and glycol monostearate) with linear chains were chosen. The economical transesterification reaction[18−20,23,18−20,25−29] was employed to introduce them into the recyclable polymers. It is easy to manipulate the transesterification ratio, namely, the amount of long side pendants along the backbone via the feed ratio of the biomass alcohols, which will well control the macroscopic mechanical performance. These biomass plastics contain a biogenic source up to 83.1 wt %, which holds promise to lower the manufacturing cost of these materials. (iii) Owing to the long linear side chains along the resulting macromolecular backbone, these polymers exhibit strong crystallization behaviors with melting points up to 92 °C, which meets the requirement for a commodity material. (iv) The crystalline polymers show enhanced mechanical properties compared to the soft poly(methyl 3-cyclopentenecarboxylate) and can be used as plastics like LDPE. (v) The polymer CP30 whose side chain came from melissyl alcohol (triacontanol) would generate bioactive components, e.g., triacontanol; thus, it is capable of producing an environmental benign effect.

■ RESULTS AND DISCUSSION

Synthesis. Melissyl alcohol also named triacontanol or beeswax alcohol is extracted from plant leaves of alfalfa hay and tea bushes.[60−62] By naturally forming esters with high fatty acid content, melissyl alcohol is widely found in insect or plant epicuticular waxes. It is commonly used as a phytohormone, i.e., plant growth regulator, and shows to be nontoxic and nonirritating to both humans and livestock.[63,64] Very similar to melissyl alcohol, laccerol is produced by hydrogenation of fatty acid methyl ester from an insect or plant. It can also function as a plant metabolite regulator and show to be environmentally benign.[65,66] Glycol monostearate is produced in quantities in industry and primarily derived from the esterification of ethylene glycol with stearic acid,[67] serving as an essential emulsifier and surfactant in various industries concerning pharmaceutical, food production, or cosmetic products. These three long-chain aliphatic alcohols are biomass-derived and chosen as preferential candidates as crystalline side chains for the polypentenamers.

Methyl 3-cyclopentenecarboxylate is a commercially available cyclopentene-based reagent. Its ring strain is calculated to be around 5 kcal/mol,[49] which was generally thought not

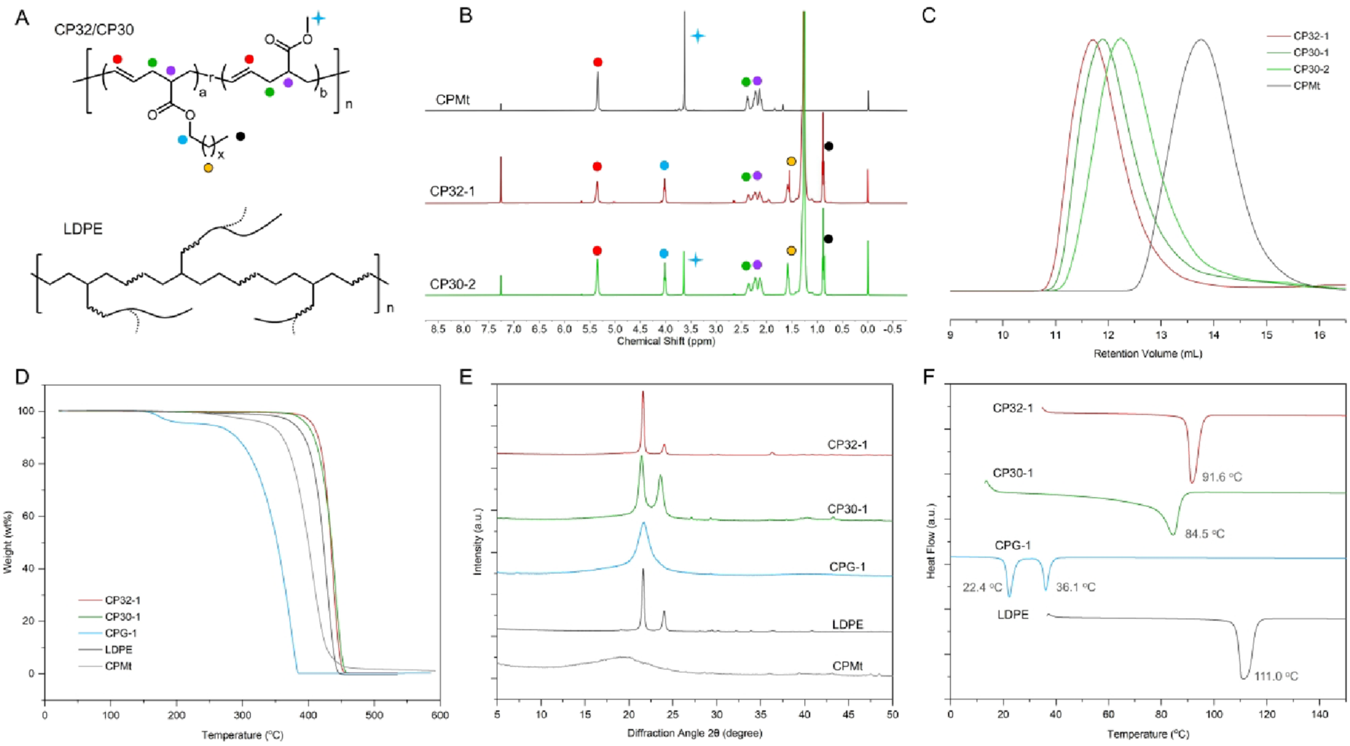


Figure 1. Synthesis of biomass-derived LDPE-like plastics. (A) Schematic presentation of CP32/CP30 and LDPE. (B) ^{1}H NMR spectra of CPMt, CP32-1, and CP30-2. $CDCl_3$ as deuterated solvent. (C) GPC chromatograms of CPMt, CP32, and CP30. (D) TGA curves for the CP polymers and LDPE. (E) WAXD patterns of CP polymers after being cooled from temperature over their melting points. (F) Second DSC melting curves. Data are rescaled and shifted vertically for clarity.

suitable for ring-opening metathesis polymerization (ROMP) strategies until highly efficient catalysts were developed.[68−71] We previously employed it as a monomer for preparation of functional polyolefins and polyethylene models.[71] The monomer conversion was up to 80%, and unreacted monomers can be recovered effectively. The polycyclopentene backbone allowed the polymer to be depolymerized under mild conditions. Based on that and the ester's potential capability for further postmodifications, we thought poly(methyl 3-cyclopentenecarboxylate) would provide an ideal platform to prepare other depolymerizable polymeric materials.

In Scheme 1, we present the synthesis route. First, the petroleum-industrially available methyl 3-cyclopentenecarboxylate was employed and polymerized to afford poly(methyl 3-cyclopentenecarboxylate) (CPMt) with a depolymerizable backbone. The Hoveyda−Grubbs second-generation catalyst (HG2) was added to initiate the ring-opening metathesis polymerization with a molar ratio 0.125 mol % of the monomer. The monomer conversion was calculated as 81%. We recovered the unreacted monomer from the precipitant solution. NMR and GPC were used to characterize the structure and molecular weight of poly(methyl 3-cyclopentenecarboxylate).

In the subsequent step, the three long-chain aliphatic biomass-derived alcohols, i.e., laccerol, melissyl alcohol, and glycol monostearate, were used to perform the transesterification reaction to replace the methyl group along the CPM side chain. Both $Ti(OBu)_4$ and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) could mediate transesterification reaction. We employed $Ti(OBu)_4$ with a feeding ratio of 1 mol % of ester units. Because these crystalline side chains probably would afford PE-like properties, to learn the effects of molar percent of repeat units containing long side chains on the properties of resulting polymers, the transesterification (TE) ratio using different feeding ratios of the three biomass-derived alcohols was probed. ^{1}H NMR spectra could determine the TE ratio as molar percent of long side-chain repeat units, which would be converted to biomass contents (wt %) and calculated to show their biomass-derived traits.

The predicted microstructure between these biomass-derived cyclopentene polymers and LDPE show a few similarities as the latter also contains a lot of long branches (Figure 1A); therefore, we envision that more properties can be simulated using these polymers. ^{1}H NMR was employed to monitor the polymerization and transesterification (Figures 1B and S1−S10). Clean ROMP to afford CPMt was determined by the signal of the internal C═C proton at 5.35 ppm upfield-shifted from 5.65 ppm assigned to the monomer's olefin bond. The configuration of the C═C double bonds in the main chain was determined by ^{13}C NMR analysis (Figure S2). Around 93% olefin carbons are characterized as *trans* configuration in CPMt. The high stereoselectivity of double bonds should be due to the fact that the HG2 catalyst could perform control well on the ROMP of low ring-strain monomers and preferentially afford high *trans* configuration.[48,69] After full transesterification, methyl (3.64 ppm) adjacent to ester groups disappeared, and instead, the methylene group previously adjacent to the hydroxyl group of alcohol that appeared at 4.01 ppm and the alkyl chain were observed at 1.25−0.88 ppm. Then, completely new polymers, e.g., CP32-1 (TE ratio >99 mol %) formed. For partially substituted polymers, e.g., CP30-2 (TE ratio 75 mol %), a few methyl groups would be reserved at 3.64 ppm (Figure 1B and Figure S7). We found that the TE reaction showed high

Table 1. Information of Polymers by Transesterification Using Poly(methyl 3-cyclopentenecarboxylate) (CPMt) and Biomass-Derived Alcohols[a]

entry	polymer	alcohol	M_n (kDa) (Đ)[b]	TE ratio (mol %)[c]	biomass content (wt %)[d]	T_d (°C)[e]	T_m (°C)[f]	ΔH_m (J/g)[f]	density (g/cm^3)
1	CPMt	methanol	41.4 (1.74)	–[g]	–	338	–	–	0.902
2	CP32-1	laccerol	183.6 (1.63)	>99	83.1	406	91.6	159	0.934
3	CP32-2	laccerol	154.4 (1.71)	86	71.5	407	89.1	133	0.930
4	CP32-3	laccerol	119.2 (1.81)	64	53.2	388	88.4	47	0.927
5	CP30-1	melissyl alcohol	162.8 (1.67)	>99	82.2	397	84.5	148	0.931
6	CP30-2	melissyl alcohol	129.9 (1.69)	75	61.7	405	82.4/69.7	113/33	0.928
7	CP30-3	melissyl alcohol	108.1 (1.70)	55	45.2	391	76.5/70.8	86	0.925
8	CP30-4	melissyl alcohol	73.7 (1.68)	24	16.5	386	68.2	59	0.918
9	CPG-1	glycol monostearate	141.3 (2.00)	>99	77.5	245	36.1/22.4	31/40	0.911
10	CPG-2	glycol monostearate	78.8 (2.57)	43	32.6	299	29.9/9.4	25/9	0.908

[a] Typical conditions: 4 g of CPMt (31.7 mmol polymer repeat units), alcohol (35 mmol), 1 mol % of TBD or Ti(BuO)$_4$, 1 mbar, 160 °C for 12 h. [b] Denoted as molecular weight (polydispersity), determined via high-temperature (150 °C) GPC (1 mL/min, 1,2,4-trichlorobenzene) using polystyrene calibration. [c] Referring to the transesterification (TE) ratio as molar percent of repeat units containing long side chains. [d] Denoted as mass percent of alcohol units (side chains) along the polymer chain. [e] Determined via TGA, given as the 5% weight loss temperature, 10 °C/min. [f] Determined via DSC, values from the second scan data; T_m is defined as the peak value, and ΔH_m also from the second melting peaks. [g] Not applicable.

efficiency as it would completely substitute the methyl groups using 1.2 equiv of long-chain aliphatic biomass-derived alcohols. To partly substitute the methyl groups, one can conduct the experiments by simply lowering the alcohol feed ratio. According to ^{1}H NMR spectra, other CP polymers transesterified using laccerol, melissyl alcohol, or glycol monostearate are characterized with TE ratios ranging from 24 to >99 mol % (Table 1 and Figures S3−S10). DOSY spectra (Figure S11) indicate successful transesterification with regard to the polypentenamer lateral groups. By GPC analysis (Figure 1C, Figures S12−S17, and Table 1), CPMt shows a molecular weight (MW) M_n = 41.4 kDa and MW distribution Đ = 1.74. CP polymers with a long side chain presented increased MWs. For example, CP32-1's MW reaches M_n = 183.6 kDa (Đ = 1.63) while CP30−2 is M_n = 129.9 kDa (Đ = 1.69). The GPC chromatograms illustrate the monomodal feature with Đ ≈ 1.7, which is consistent with that of CPMt. Postmodification may change the shape slightly, which should be attributed to the different solubility and hydrodynamic dimension in the GPC eluent phase.

Properties. Thermal stability was investigated by thermogravimetric analysis (TGA). We heated the samples from RT to 600 °C at a rate of 10 °C/min with N$_2$ purging (60 mL/min). Figure 1D and Figures 18−S20 show the weight−temperature curves. These CP polymers displayed higher thermal degradation temperatures than CPMt except CPG polymers. A stage around 200 °C appeared for CPG-1, which may be due to degradation of the ethylene glycol units. This can be confirmed by the fact that CPG-2 (43 mol %) with a lower TE ratio using glycol monostearate exhibited better thermal stability than CPG-1 (>99 mol %). A longer alkyl chain would endow enhanced thermal stability, which is similar to even better than polyethylene (LDPE employed as comparison, T_d = 378 °C).

It is expected that incorporation of long side chains would afford PE-like crystallization behaviors and thus improve mechanical properties. We employed wide-angle X-ray diffraction (WAXD) patterns to determine the crystallization (Figure 1E and Figures S21−S23). For CP32 polymers and C30 polymers, two diffraction peaks are discerned at 2θ 21.21−21.50° and 24.18−24.34°, respectively. Taking commercial LDPE as a comparison, these two distinct diffraction peaks should correspond to the (110) and (200) crystal planes of orthorhombic crystal.[72] CPMt shows a fully amorphous state with a broad halo peak. These findings illustrate that PE-like alkyl side chains have the same crystal structure as common PE and that the polycyclopentene backbone does not alter the crystal structure. The exceptional crystallization fashion comes from CPG (Figure 1E and Figure S23). They only present a single diffraction peak at 2θ 21.7°, corresponding to the (110) crystal plane. It is explained that crystal growth along the (200) direction was severely suppressed, and obstacles from the polycyclopentene backbone on the side alkyl chain's movement and packing should account for that.

Bearing the crystallization information in mind, we then turned to differential scanning calorimetry (DSC) analysis (Figure 1F, Figures S24 and S25, and Table S1) to learn the thermal properties. The first cooling run and second heating run were collected, where the first heating run was to eliminate the thermal history. CPMt's glass transition temperature was detected at −25 °C (Figure S24). Predictably, a higher TE ratio, namely, higher biomass content, would endow the polymer clear crystallization and melting peaks. For instance, CP32-1 exhibits a melting peak at 91.6 °C while CP32-2 exhibits a melting peak at 89.1 °C and CP32-3 exhibits a melting peak at 88.4 °C, suggesting a slight decrease in melting points with decreased content of long alkyl side chains. However, the enthalpy declines significantly from 159 to 47 J/g, indicative of the substantially decreased crystallinity. Similar phenomena appeared for CP30 polymers. Double- or multi-melting peaks would occur concurrently for CP30 polymers with a lower content of the alkyl side chains. Clear-cut double melting peaks are likewise detected for both CPG-1 and CPG-2 with lower melting points compared with those of CP32 and CP30. It is assumed that crystals with distinct thicknesses may be formed and lead to unequal melting behaviors. We employed commercial LDPE as comparison whose melting point is 111 °C (Figure S24). Our biomass-derived polymers exhibit little low melting points, but these melting disparities are found to have few influences on the material's mechanical performance, as determined in the following section.

Promisingly, these biomass-derived cyclopentene-based polymers could exhibit similar mechanical performance with

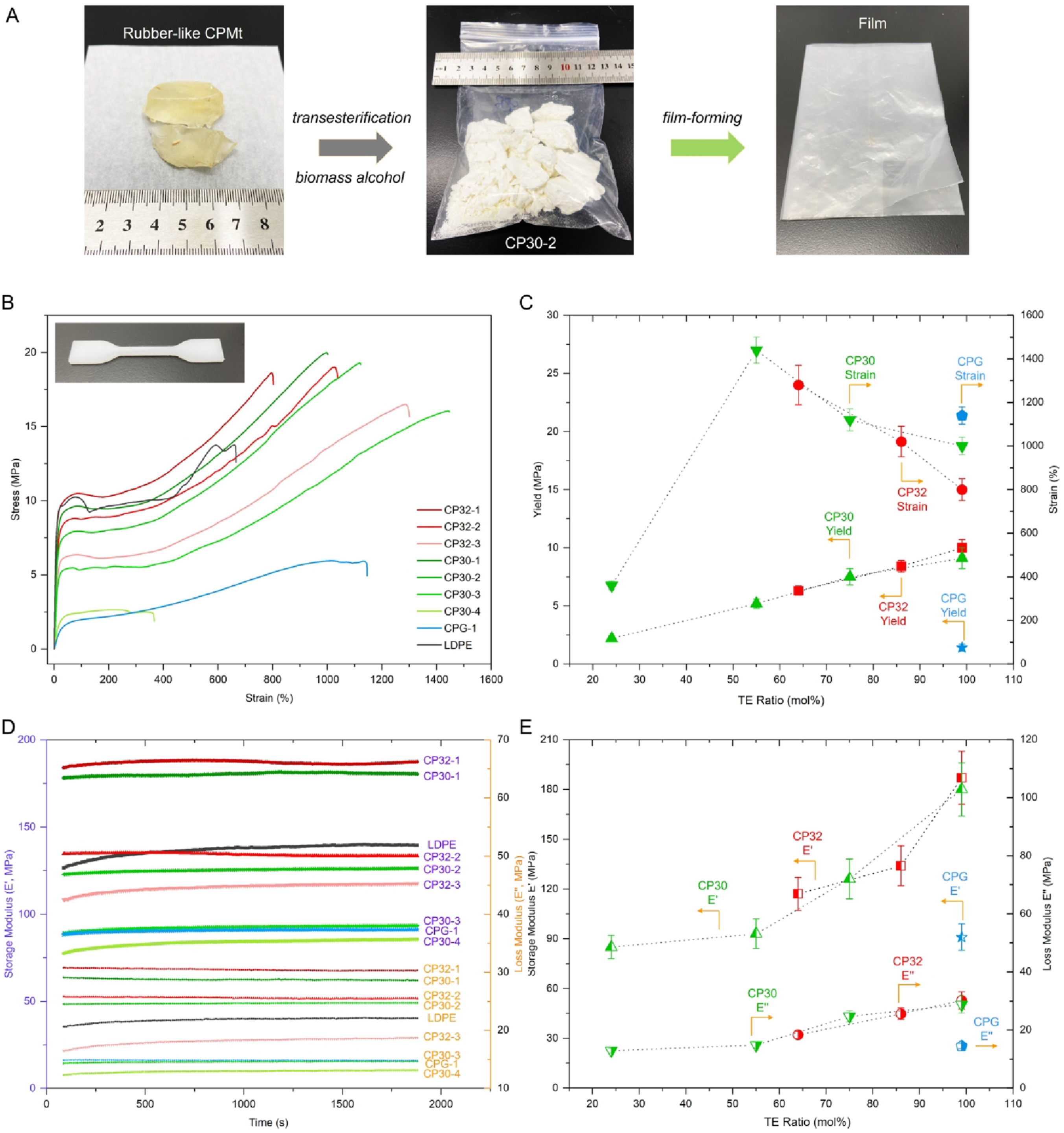


Figure 2. Probing the macroscopic properties of biomass-derived LDPE-like plastics. (A) Photographic images of rubber-like CPMt, CP30-2 solid product, and film sample (thickness ~ 0.12 mm). (B) Stress−strain curves and (C) relationships between yield/strain and transesterification (TE) ratio. (D) DMA test results and (E) relationships between the storage modulus E'/loss modulus E'' and transesterification (TE) ratio.

polyethylene, since they contain a large volume of crystalline PE oligomer pendants. We thus probed their tensile properties and compared them with commercial LDPE. Figure 2A shows the phenotype that rubber-like CPMt was transformed into the plastic CP30-2. CP32, CP30, and CPG specimens for the tensile stress−strain test were prepared by hot compression using a plate vulcanizing machine and stainless-steel die molds for standard dog bone samples. The compression was conducted at 160 °C under 10 MPa pressure for 15 min, and then the specimens were cooled to room temperature. After 48 h, uniaxial tensile elongation experiments were carried out at RT and with a tensile rate of 50 mm/min. Specimens (length × width × thickness 20 × 6 × 0.5 mm^3) for dynamic mechanical analysis (DMA) were made using a similar processing. Measurements were made by an instrument equipped with dual cantilever geometry at RT (25 °C) with a frequency of 1 Hz and an amplitude of 20.0 μm.

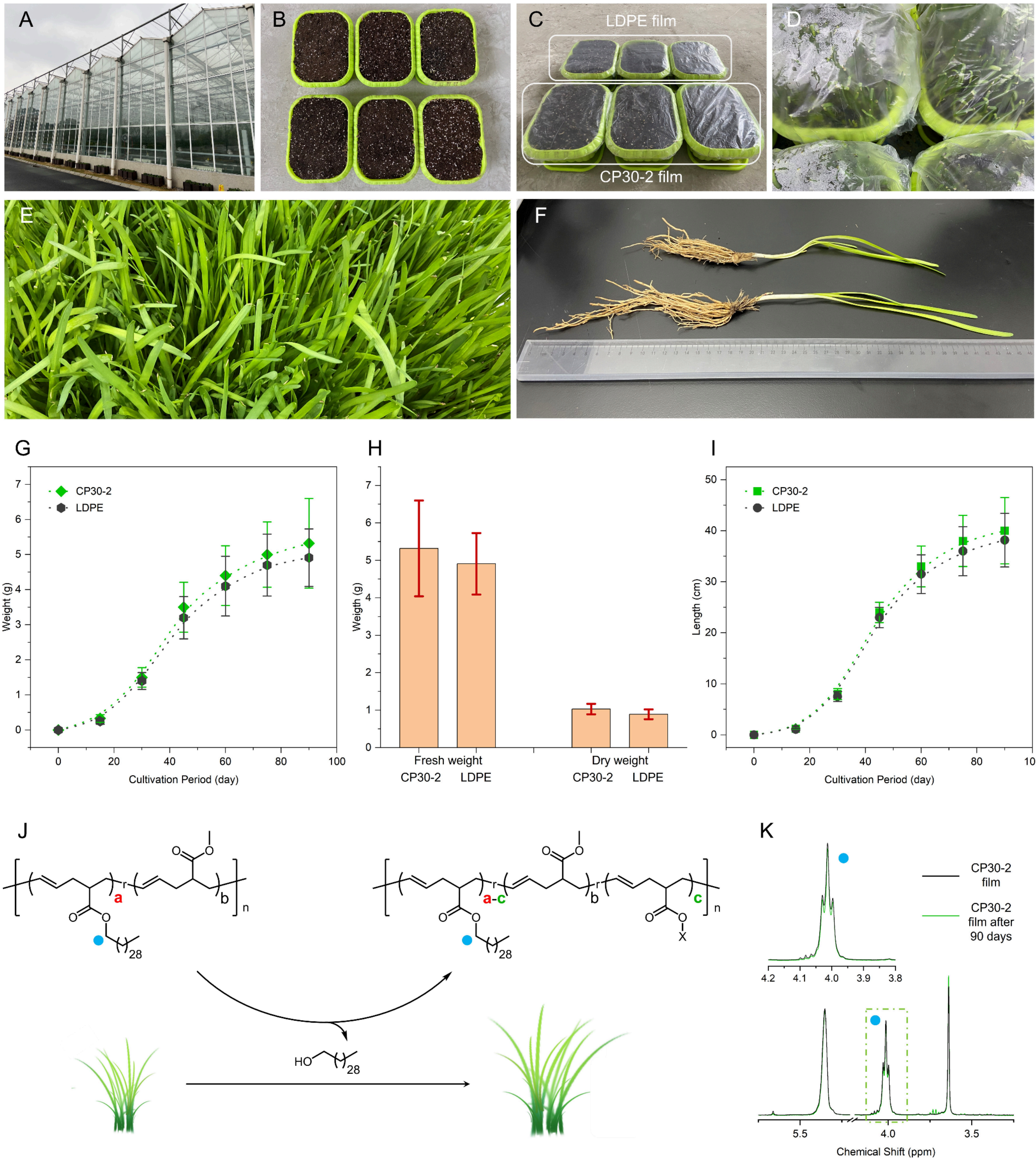


Figure 3. Cultivation process of the leafy vegetable (*Allium tuberosum* Rottler ex Spreng) under standard conditions. (A) The green house had a consistent temperature (daytime 25 °C/nighttime 18 °C) and humidity (75% RH). (B) Petri dishes (33 × 24.5 × 13.5 cm). (C) Three of the Petri dishes were film-covered using CP30-2, while the other three ones were covered using the LDPE film. After (D) 45 days and (E) 75 days, seedlings showed normal growth. (F) Photo of mature chives after 90 days and length measurement. (G) Weight change and comparison between samples using CP30-2 and LDPE films, respectively. (H) Weight histograms for fresh weight and dry weight. (I) Length change and comparison between samples using CP30-2 and LDPE films, respectively. (J) Proposed release of triacontanol and promotion of the leafy vegetable. (K) Changes of the peak assigned to side chain in the stacked NMR spectra.

In Figure 2BC and Figures S26−S28, we find that the tensile behaviors of CP32 and CP30 samples with transesterification (TE) ratio >75 mol % are more similar to that of LDPE, with yield points ranging from 7.5 to 11 MPa and a strain at break of 800% for CP32-1, 1020% for CP32-2, 1000% for CP30-1, and 1120% for CP30-2, compared with LDPE (660%). The apparent better elongation performance should be attributed to the increased chain flexibility due to the large content of olefinic bonds in the main chain. With lower TE ratios (Figure 2C), such as 64 mol % of CP32-3 and 55 mol % of CP30-3, the yield points would decrease to 6.3 and 5.2 MPa, respectively. Much lower TE ratios like CP30-4 (24 mol %) lead to remarkably weakened tensile behavior. For CPG with shorter side chains, their tensile properties are a little poor and more like some polyolefin rubber or elastomer without vulcanization, while CPG-2 did not take shape into standard specimens for tensile test primarily due to its low crystalline pendant content. These results reveal the well regulable mechanical performances via a qualitative option of the alcohols or a quantitative TE ratio.

For DMA measurement, the storage modulus E'/loss modulus E'' of CP32-1 and CP30-1 are 187 MPa/30.2 and 180 MPa/28.8 MPa, respectively, much larger than that of LDPE (138 MPa/22.0 MPa) (Figure 2DE). The samples with E's/E''s that are approximate to LDPE are CP32-2 (134 MPa/25.6 MPa) and CP30-2 (126 MPa/24.7 MPa). The storage modulus E'/loss modulus E'' of CP32-3 (117 MPa/18.3 MPa) decreases a little, while CP30-3, CP30-4, and CPG-1 with E'/E'' around 85−93 MPa/12.9−14.8 MPa decrease significantly, suggesting their different mechanical performance from LDPE. We then employed the CP30-2 sample for further application studies. CP30-2 containing 75 mol % long alkyl side chains (61.7 wt % biomass) can be more easily accessed compared to CP32-1 and CP30-1 with a TE ratio of 100 mol %. We measured the water vapor and water permeability of the CP30-2 film (Figure 2A). The water vapor permeability at 40 °C is 2.74 g/(m^2 × 24 h), while water permeability cannot be detected at RT for the films. This would endow the film with a high soil moisture conservation property. The oxygen permeability test was made at RT, and the value 0.15 cm^3/(m^2 × 24 h) was acquired.

Application Concerning Biological Activity. In agriculture, it is found that there are many challenges to effectively utilize natural or synthetic plant growth regulators (PGRs) at present.[62−64] One of the notable practical limitations is their poor water solubility, which often necessitates the use of a large amount of environmentally detrimental organic media. The limited suspension in water would also prevent their effective dispersion over the crop leaves as well as roots. Recently, people have made great efforts on that using nanotechnology. These nanoparticles can act as carriers to deliver PGRs efficaciously.[64] For polymers CP32 and CP30, since they have the potential to be biodegraded into PGRs laccerol (dotriacontanol) or melissyl alcohol (triacontanol), we would regard them as the simple sustained-release drug delivery system. In the ecosystems, the degradation products laccerol and melissyl alcohol can facilitate growth of plants. For instance, it has been demonstrated that triacontanol can regulate various physio-biochemical processes, e.g., salinity stress, leading to increased nutrient intake, photosynthesis efficiency, and so forth, thus finally boosting plant growth and stimulating productivity.[62−64]

Accordingly, we turned to learn the application of CP30 as agricultural shed films or mulch films to probe its more functions not limited to being films for single-purpose use. We made the films by using a plate vulcanizing machine instead of extrusion blow molding. The specimens were prepared at 160 °C under 10 MPa pressure to afford a thin film with thickness of ∼0.12 mm. Control samples using LDPE film (thickness ∼0.12 mm) were purchased from commercial corporations (raw material was from Sinopec LDPE 2426K). The films were employed to assist the cultivation of leafy vegetables, e.g., *Allium tuberosum* Rottler ex Spreng at standard conditions (temperature daytime 25 °C/nighttime 18 °C, humidity ∼75% RH and indoor) (Figure 3A). Under other natural conditions including ultraviolet rays, oxygen, and other trace substances from soil, we simulated that to probe the effects of CP30 mulch films on the plant growth, if any. The plant's weight and length changes were tracked and recorded using dozens of samples in different Petri dishes. Photographic records are presented in Figure 3B−E and Figure S29 and revealed that seedling exhibited normal growth.

The photographs of the *Allium tuberosum* Rottler ex Spreng mature samples are presented in Figure 3F. We weighed the samples by balance using their fresh and fully dried statuses, respectively. The samples were dried at 80 °C in a vacuum oven to consistent weights. Representative weight data for samples cultivated using CP30-2 films are shown in Tables S2 and S3. We measured the length of the stem leaves, since they are the edible portion. Weights including fresh and dry weights and lengths for samples cultivated by CP30-2 films and LDPE films respectively were compared, as shown in Figure 3G−I and Figures S30 and S31. We found that they showed a slightly similar growth tendency while samples using the CP30 mulch film exhibited a little better than that using the commonly used LDPE film. For instance, we weighed the mature crops that were suitable for cooking. It is found that the fresh weight (W_n^{fresh} = 5.32 g, $W_w^{\text{fresh}}/W_n^{\text{fresh}}$ = 1.02) of samples using CP30 mulch films shows to be higher than that using LDPE films (W_n^{fresh} = 4.91 g, $W_w^{\text{fresh}}/W_n^{\text{fresh}}$ = 1.02). A similar result was obtained for the dry weights (W_n^{dry} = 1.03 g, $W_w^{\text{dry}}/W_n^{\text{dry}}$ = 1.02) compared with that (W_n^{dry} = 0.89 g, $W_w^{\text{dry}}/W_n^{\text{dry}}$ = 1.02) using the LDPE film. This can also be verified by the fact that the length (L_n = 40.13 cm, L_w/L_n = 1.03) was longer than that (L_n = 38.17 cm, L_w/L_n = 1.02) using the LDPE film with 200 specimens traced. Therefore, the CP30-2 film was more conducive to the growth of *Allium tuberosum* Rottler ex Spreng than the commercial LDPE film.

The improvement of production (ΔW^{fresh} = 0.41 g and ΔW^{fresh} = 0.14 g) will be more considerable when it is calculated using larger-scale application since 200 samples herein have already increased the production by 82 g. The increased crop production should be attributed to the film containing the PGR chemical component. With 90 days, there should be very few cleavages of esters along the CP30-2 backbone (Figure 3JK and Figures S7 and S32), even though no catalysts were employed except the ultraviolet rays, oxygen, and moisture and some unknown agents in the earth may function to accelerate the cleavage or not. More studies are needed to develop a strategy to cleave the ester groups and release the PGR, e.g., triacontanol (melissyl alcohol) in a well-controlled fashion, in which larger improvement of crop production can be expected.

Degradation and Reuse. Very few cases appeared to show that commercially available Grubbs catalysts can efficiently initiate the depolymerization of a series of recyclable polypentenamers.[45,48] We herein presented that the polymers could be fully converted into the original monomers. These monomers were able to repolymerize into polymers. For polymers CP32 and CP30, their corresponding cyclopentene-based monomers (dotriacontyl 3-cyclopentenecarboxylate and triacontyl 3-cyclopentenecarboxylate) are favorably useful and can be ring-opened for polymerization, regardless of their strong crystallization leading to low conversion under the

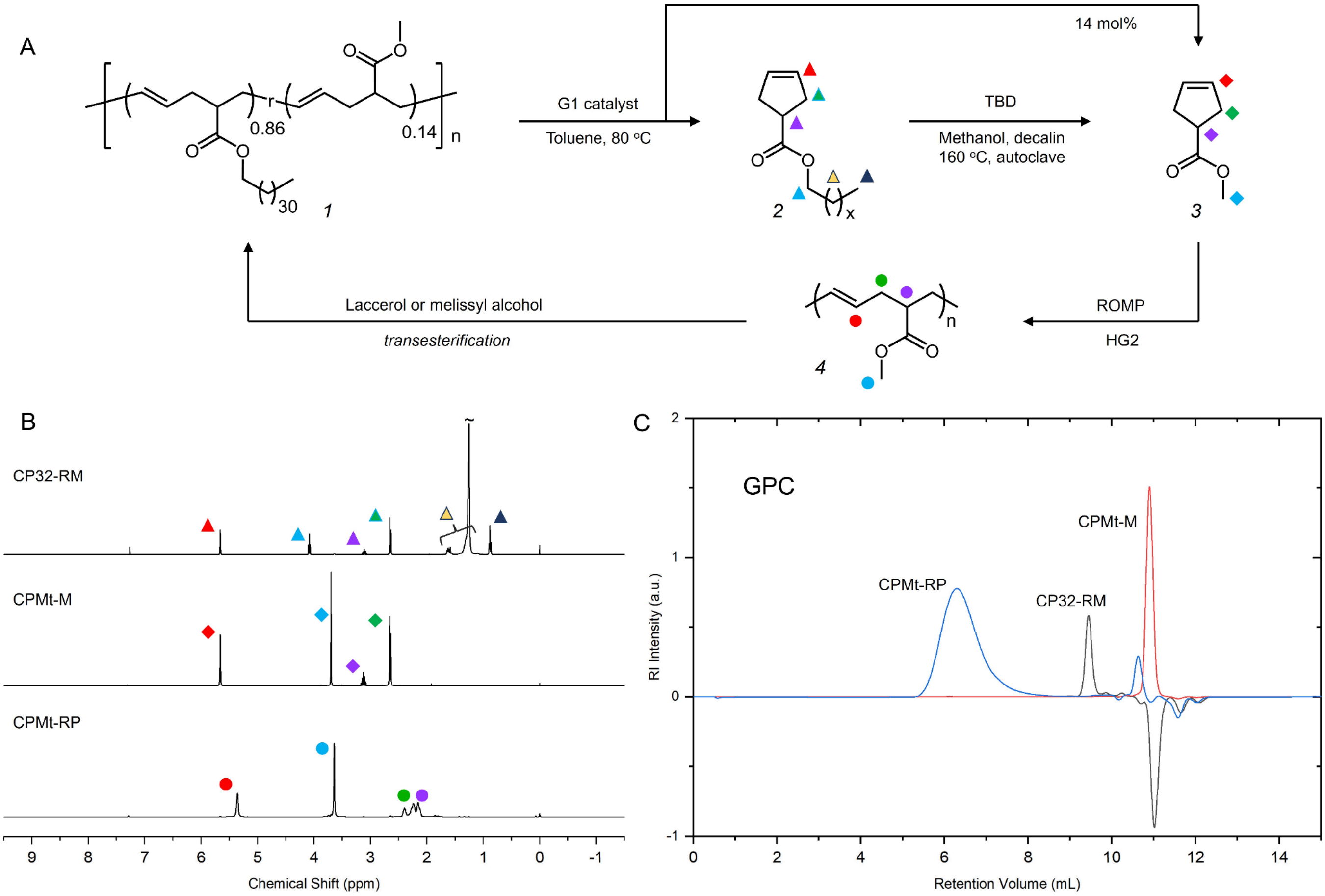


Figure 4. Full closed-loop recycling of the biomass-derived polymer. (A) Scheme of the depolymerization of CP32-2 to its corresponding cyclopentene-based monomers. Transesterification of them to afford methyl 3-cyclopentenecarboxylate, which is employed to repolymerize to access CPMt. CPMt can be transformed to CP32. (B) ^{1}H NMR spectra and (C) GPC chromatograms to track the CP32-2 depolymerization. $CDCl_3$ as deuterated solvent (25 °C) and THF at 40 °C as the eluent, respectively.

polymerization conditions. Nevertheless, these monomers are not commercially available and need artificial synthesis using 3-cyclopentene-1-carboxylic acid and the corresponding alcohols. It is envisaged that CP32 and CP30 are first depolymerized into small molecular monomers, and then these cyclopentene-derived monomers are collected for further use or transformed into other cyclopentene-based monomers. To simplify the protocol, we took the inverse transesterification into methyl 3-cyclopentenecarboxylate as an example (Figure 4A). CP32-2 was dissolved into toluene at an ~0.1 M concentration of polymer repeating units. The Grubbs first-generation catalyst (G1) was added with 0.5 mol %. Then, the solution was heated to 80 °C for 2 h. The reaction mixture was precipitated into acidic methanol, and the degradation product CP32-RM was obtained. The methyl 3-cyclopentenecarboxylate was collected from the methanol solvent by evaporation and distillation.

^{1}H NMR spectra and GPC chromatograms (Figure 4BC and Figures S33 and S34) confirmed the successful depolymerization. No polymer residuals were detected, implying full degradation of polymer CP32-2 1. Subsequently, CP32-RM 2 (R refers to recovered and M as monomer) was dissolved in decalin, and TBD (2 mol %) and excess methanol were added. Heating the mixture at 160 °C for 24 h resulted in 95% conversion of ester linkages into methyl 3-cyclopentenecarboxylate 3 (CPMt-M). The lacccerol was recovered from the precipitants in methanol. In Figure 4B, the ^{1}H NMR spectrum of CP32-RM with seven distinct protons at 5.66, 4.08, 3.11, 2.65, 1.62, 1.24, and 0.88 ppm is quite different from that of the CP32 polymer. After degradation and TBD transesterification, methyl 3-cyclopentenecarboxylate was collected by distillation and purified. Its ^{1}H NMR spectrum (Figure 4B) indicates the complete transformation from CP32-RM 2, where the methylene unit adjacent to the *O* atom of the ester group was changed to methyl at 3.69 ppm. GPC chromatograms in Figure 4C demonstrate that CP32-RM 2 and CPMt-M 3 contained no polymers and were pure after degradation and TBD transesterification respectively, while poly(methyl 3-cyclopentenecarboxylate) 4 (M_n = 78.8 kDa, $Đ$ = 2.05) (CPMt-RP, RP denotes as recycled polymer) was successfully obtained by repolymerization of CPMt-M (Figure S35). The recovered lacccerol or melissyl alcohol subsequently was able to transform poly(methyl 3-cyclopentenecarboxylate) 4 to prepare CP32 or CP30, realizing full closed-loop recycling.

For CPG, one could take another perspective on their recyclability. The ethylene glycol units along the side chain allow more functional groups to be introduced by the transesterification reaction. Bromide group has been used to transform polymers into zwitterionic and electrolyte materials.[73] Alkyne group is proved to be the favorable building block along polymer backbone to perform Cu(I)-catalyzed azide−alkyne click coupling reaction.[74] −Si-O- containing polymers are important adhesive materials.[75] Herein we would like to

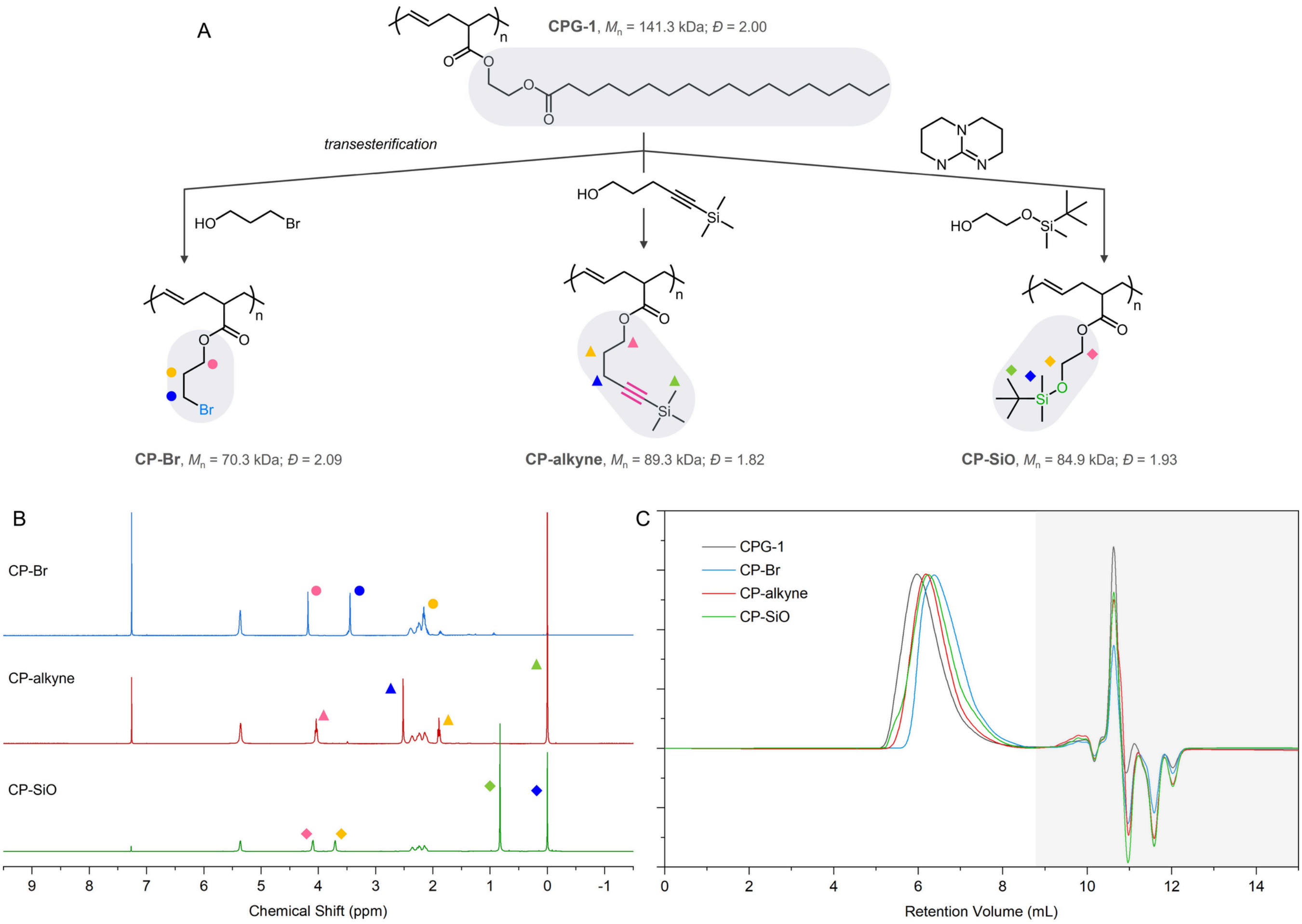


Figure 5. Postfunctionalization of CPG. (A) Scheme of postmodifying CPG to afford CP-Br, CP-alkyne, and CP-SiO by transesterification. (B) ^{1}H NMR spectra and (C) GPC traces of postfunctionalized products. $CDCl_3$ as deuterated solvent (25 °C) and THF at 40 °C as the eluent, respectively.

transform CPG into these three functional polymers containing bromide, alkyne, and −Si-O- groups, respectively (Figure 5A). Specifically, to suppress the gelation due to cross-linking from diols and ester units along the polymer backbone, excess 3-bromo-1-propanol, 5-(trimethylsilyl)pent-4-yn-1-ol and 2-((*t*-butyldimethylsilyl)oxy)ethanol were added to substitute the side chains in the presence of TBD at 140 °C.

^{1}H NMR spectra verify the successful transformation (Figure 5B and Figure S36) with the disappearance of peaks assigned to the long side chains at around 1.26 ppm. Instead, methylene units adjacent to the *O* atom of the ester group are detected at 4.18 ppm for CP-Br, 4.04 ppm for CP-alkyne, and 4.10 ppm for CP-SiO. Other characteristic peaks, for instance, methylene adjacent to the Br atom appearing at 3.44 ppm, methyl units of CP-alkyne's trimethylsilyl group at 0.00 ppm, and similarly, methyls of CP-SiO's trialkylsilyl group, are located at 0.83 and 0.00 ppm, respectively. The conversion to bromide, alkynyl, and −Si−O− pendants can be over 99% since very few signals from CPG-1 were observed. The MWs were decreased reasonably due to removal of long alkyl side chains (Figure 5C), for instance, M_n = 141.3 kDa (Đ = 2.00) for CPG-1 and M_n = 70.3 kDa (Đ = 2.09) for CP-Br, M_n = 89.3 kDa (Đ = 1.82) for CP-alkyne, and M_n = 84.9 kDa (Đ = 1.93) for CP-SiO, while their molecular weight distributions (Đs) remained at the approximate values. The −Si−O− group is moisture sensitive and easily hydrolyzed to form hydroxyl. The formation of the hydroxyl unit would lead the intermolecular cross-linking, thus affording a few components that show a much higher molecular weight. The successful postfunctionalization to access functional polymers demonstrated the reusability of these biomass-derived plastics.

■ CONCLUSIONS

The protocol to synthesize polypentenamers through transesterification here provides a way to manufacture recyclable polymeric plastics. The controlled transesterification ratio allowed for preparation of a series of polycyclopentene-based polymers containing biomass alcohol units ranging from 24 to >99 mol % while mass percent ranged from 32.6 to 83.1 wt %. The linear alkyl side chain from biomass alcohols endowed the polymers enhanced thermal stability and crystallization behaviors with sufficiently high melting points. The orthorhombic crystals due to the linear PE oligomer-like side chain are similar to those of PE. Above the transesterification ratio of around 60 mol % for both CP32 and CP30 using laccerol and melissyl alcohol with biomass content above 50 wt %, the resulting polymer would exhibit mechanical performances comparable to commercial LDPE. We employed a representative polymer CP30-2 (transesterification ratio, 75 mol %; biomass content, 61.7 wt %) to learn its practical applications. We found that it can be used as a film material counterpart of LDPE for cultivation of leafy crops. More noteworthy is that it would probably release a few melissyl alcohol (triacontanol). This biologically active natural product is able to act as a plant growth regulator to increase the crop yield, suggesting that several new favorable properties can be concurrently introduced into a single polymeric material. We conducted the depolymerization of biomass plastics using the 0.5 mol % catalyst and the polymerizable monomers can be completely recovered, realizing a full closed-loop recycling. Further postfunctionalization allowed for more reuse possibilities. Future studies will focus on exploring the scope of these biomass plastic's sustainable applications.[76−78]

■ ASSOCIATED CONTENT

Data Availability Statement

All data generated during the study are available in the Supporting Information. This study did not generate a code.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.5c01976.

> Materials and instrumentation, experimental details including transesterification, cultivation of leafy crop, degradation, and postfunctionalization (PDF)

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Notes

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