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Brown Grease as a Precursor to Polyol Monomer for Polyurethane Synthesis

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The valorization of waste-derived feedstocks for polymer synthesis represents a sustainable alternative to petroleum-based materials. In this study, brown grease, a low-value waste lipid source, is utilized as a precursor for polyol monomer synthesis via a two-step functionalization process. Transesterification of brown grease with allyl alcohol generates allyl esters, which are subsequently modified via thiol-ene click chemistry with 2-mercaptoethanol to yield hydroxyl-functionalized polyols (**BG-diol**). The thiol-ene reaction proceeds under mild UV-initiated conditions, achieving high conversion efficiency (>90%) while preserving the structural integrity of the derived polyol. **BG-diol** is further polymerized with 4,4′-methylene diphenyl diisocyanate (MDI) through step-growth polymerization to form brown grease-derived polyurethane (**BG-PU**). Comparative analysis of **BG-PU** with polyurethane (PU) synthesized from purified oleic acid (**OLA-PU**) demonstrates comparable molecular weight distributions (M_n = 14.4 kDa, M_w = 20.4 kDa for **BG-PU**) and thermal properties (T_g = 24 °C, $T_{d,5\%}$ = 270 °C for **BG-PU**). These results underscore the feasibility of brown grease as a cost-effective and renewable alternative to plant oil-based polyols, offering a pathway toward sustainable PU production while mitigating food security concerns. This approach exemplifies the potential of waste lipids in circular economy strategies for high-performance polymer synthesis.

1. Introduction

The growing emphasis on sustainability in materials science has led to increased interest in developing polyurethanes (PUs) derived from renewable feedstocks.[1–7] One promising approach has been using plant oils as a source of renewable monomers.[8–12] Vegetable oils such as soybean,[13–17] castor,[18–21] and palm oils[22–24] contain triglycerides rich in unsaturated fatty acids, which can be chemically modified to introduce hydroxyl functionalities, allowing them to serve as polyol precursors for PU synthesis.[8,25]

Among the many strategies for converting plant oils into PU monomers, thiol-ene "click" chemistry has gained attention due to its high efficiency, functional group tolerance, and ability to produce well-defined structures.[26–38] The thiol-ene reaction involves the addition of a thiol (–SH) to a carbon–carbon double bond under radical initiation, typically using light or thermal activation. This reaction is particularly well-suited for modifying unsaturated fatty acids derived from plant oils, as the naturally occurring double bonds provide reactive sites for thiol addition. Researchers have successfully developed bio-based diols that can be further polymerized into PUs by functionalizing these fatty acids with hydroxyl-containing thiols.

The thiol-ene reaction offers several advantages in the context of sustainable monomer synthesis. Unlike other functionalization methods, which may require harsh conditions, toxic reagents, or multiple reaction steps, thiol-ene chemistry proceeds under mild conditions, often using low-energy LED lights to initiate the reaction and exhibits excellent selectivity. This eliminates the need for excessive purification and minimizes byproduct formation, making the process more environmentally friendly. Additionally, the reaction is highly versatile, allowing for precise control over monomer structure and functionality. Unlike other sulfur radical-based strategies like inverse vulcanization of plant oils to give high sulfur-content materials, the polymers produced by the thiol-ene reaction are predominantly organic in nature, and exhibit properties similar to traditional commodity organic polymers. Given these benefits, thiol-ene chemistry has been widely explored for developing renewable PU precursors, offering a viable alternative to petrochemical-based synthesis.

Despite these advancements, a major limitation of bio-based PU production remains the cost and availability of high-purity fatty acids or plant oils used as feedstocks. Furthermore, using nutritionally valuable plant oils on large scales to supplant petrochemical plastic production would contribute to food scarcity and insecurity. To address this challenge, we propose a more sustainable and cost-effective approach by replacing plant oils with brown grease—a low-value, high-fat waste product derived from used cooking oils, restaurant grease traps, and fat-rendering industries. Brown grease is rich in free fatty acids and can be chemically modified analogously to plant oils, offering a practical

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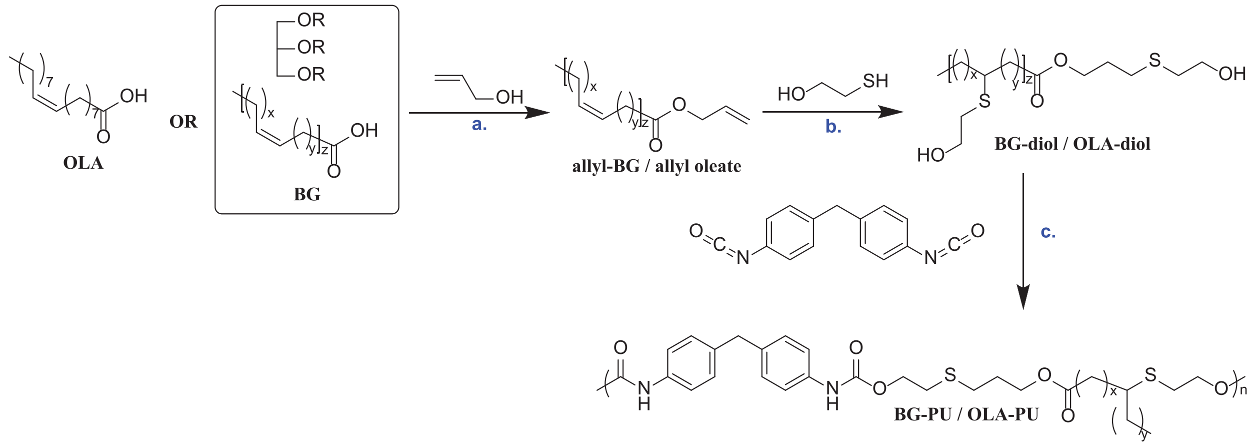

Scheme 1. Synthetic routes to target PUs from oleic acid and brown grease: a) esterification or transesterification, b) thiol-ene addition, and c) step-growth polymerization with MDI. R groups represent fatty acid chains.

alternative. Furthermore, contaminants found in brown grease preclude its consumption by humans or its use in animal feed, so its use for plastic production will not contribute to food insecurity. Brown grease is already produced as a waste product, so its utility does not require agricultural land. A 2020 National Renewable Energy Laboratory study estimated that brown grease costs \$100 USD per dry metric ton, compared to ~\$1000 USD per ton of soybean oil, emphasizing the significant economic advantages of using this low-value fat source in place of plant oils.[39]

In this study, brown grease is converted to polyol monomers by transesterification with allyl alcohol followed by thiol-ene reaction with 2-mercaptoethanol, giving **BG-diol**. Polymerization of **BG-diol** with 4,4′-Methylene diphenyl diisocyanate gave brown grease-derived polyurethane (**BG-PU**). Comparison of the properties of **BG-PU** to those of the analogous PU prepared from pure oleic acid reveals the viability of this method for using brown grease in place of plant oils or even purified fatty acids.

2. Results and Discussion

The brown grease used in this study has 34% free fatty acids, 0.57% moisture, and 0.81% unidentified impurities, with the balance being a mixture of glycerides. Brown grease composition can vary significantly in the free fatty acid content, from ~10% to over 50%. In the current case, a brown grease sample with a free fatty acid content of 34% was used. This variability is offset by the synthetic strategy selected for this study because all free fatty acids as well as fatty acid chains found in monoglycerides, diglycerides, and triglycerides in the initial brown grease sample are converted to allyl esters. This brown grease sample was converted into allyl esters through *p*-toluenesulfonic acid-catalyzed transesterification with allyl alcohol (Scheme 1). The transesterification reaction proceeded efficiently under mild conditions to yield a mixture of allyl esters. Simple liquid–liquid extraction and removal of volatiles gave **allyl-BG** as a mixture of fatty acid allyl esters with an olefin content of 1.48 mmol/g of material. The **allyl-BG** was used in subsequent steps without further purification (Figure 1, full spectra provided in Figure S1).

Allyl-BG was subjected to thiol-ene click chemistry using 2-mercaptoethanol to introduce hydroxyl functionalities, yielding **BG-diol**. This reaction proceeded under UV light initiation with 2,2-dimethoxy-2-phenylacetophenone (DMPA) as the photoinitiator. Although **allyl-BG** is a mixture of allyl esters, the conversion to **BG-diol** was very efficient (90.7% yield based on theoretical conversion of all olefins), reflecting the well-known efficiency, high yield, and functional group tolerance of the thiol-ene reaction (Figure 1). The successful transesterification of brown grease can be seen through the appearance of new olefinic and methyl ester protons, attributable to the allyl ester moiety, at 5.93, 5.23, and 4.58 δ (ppm) on the ^{1}H NMR spectrum, respectively, (Figure 2b, full spectra provided in Figures S2–S6). The disappearance of the glycerol backbone protons from the triglyceride components of the brown grease around 4.30 – 4.00 δ (ppm) demonstrated the robustness of the acid-catalyzed transesterification in converting both fatty acid and triglyceride components within the brown grease into the desired mixture of allyl esters (Figure 2). Furthermore, the efficiency of the thiol-ene reaction with **allyl-BG** was observed by the disappearance of all respective olefinic protons and the appearance of new methylene protons at 3.73, 2.73, and 2.60 δ (ppm), attributed to the thioether bond formation, demonstrating $\geq$ 95% conversion to the desired mixture of polyols (Figure 2).

To evaluate the feasibility of using brown grease-based polyols in PU synthesis, **BG-diol** was polymerized (Scheme 1) with MDI (4,4′-methylene diphenyl diisocyanate) following the same procedure reported for **OLA-diol**. We also carried out polymerization of **OLA-diol** to form **OLA-PU** under identical conditions to allow for a direct comparison of the materials. For this polymerization, an isocyanate index (NCO:OH ratio) of one was used, where the alcohol content of the **BG-diol** mixture was based on the NMR data. The polymerizations proceeded in DMF solution using tin (II) 2-ethylhexanoate as a catalyst at 50 °C for 24 h. The resulting thermoplastic PUs, **BG-PU** from **BG-diol** or **OLA-PU** from **OLA-diol**, were isolated via precipitation and drying, yielding a light brown or white solid, respectively. The resulting **BG-PU** was obtained as a soft, elastic solid that retained its shape under ambient conditions, but deformed slightly under moder-

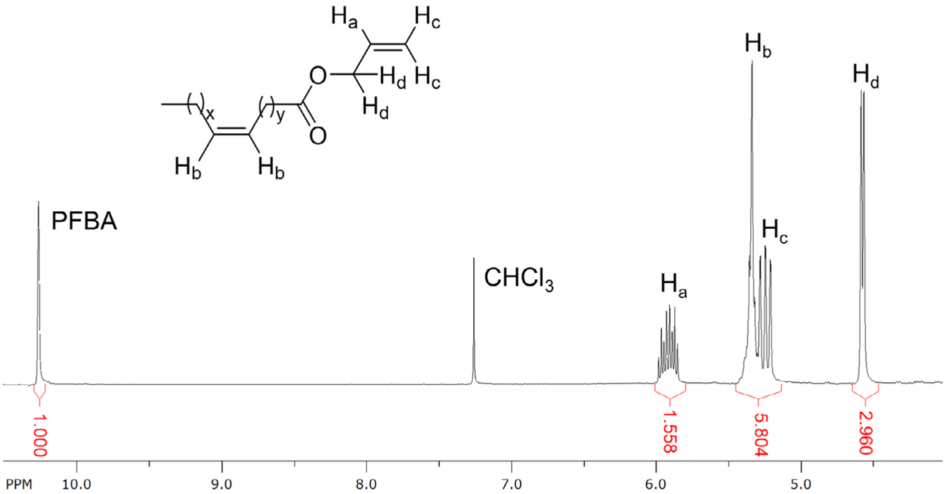

Figure 1. Proton NMR spectrum (300 MHz, $CDCl_3$) of **allyl-BG** with 2,3,4,5,6-pentafluorobenzaldehyde (PFBA) as the internal standard. Quantification of olefin content in mmol/g of material was calculated in reference to H_b and H_c protons. Olefin content was calculated as 1.48 mmol/g of material.

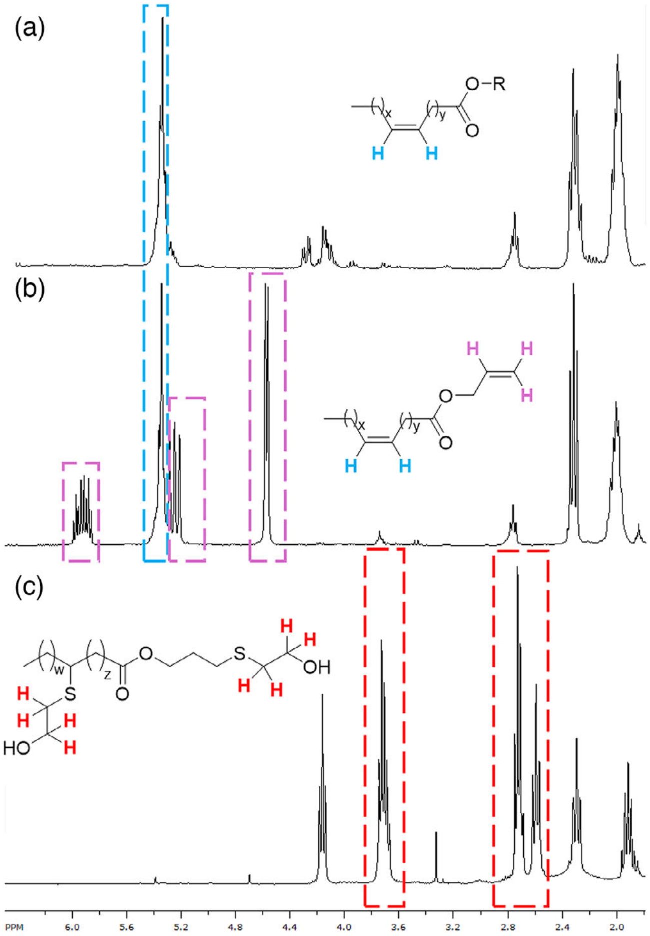

Figure 2. Proton NMR spectra of a) brown grease, b) **allyl-BG**, and c) **BG-diol**. Dashed boxes represent the proton signals corresponding to the olefins (blue and purple) and methylene units from the thioether substituent (red).

Table 1. GPC, thermal, and mechanical data for **OLA-PU** and **BG-PU**. Molecular weight properties determined through gel permeation chromatography. Thermal properties reported as temperature at 5% weight loss ($T_{d,\ 5\%}$), mass of residue remaining at the end of TGA at 800 °C (char yield), and glass transition temperature (T_g). Mechanical properties reported as elongation at break, ultimate tensile strength (UTS), and Young's modulus.

Properties	OLA-PU	BG-PU
M_n/kDa	19.4	14.4
M_w/kDa	28.4	20.4
$Đ$	1.46	1.42
$T_{d,\ 5\%}$/°C	267	270
Char yield/wt. %	1.74	2.41
$T_{g,\ DSC}$/°C	15	24
Elongation at break/%	62.9 ± 0.2	59.9 ± 0.6
UTS/MPa	1.35 ± 0.02	1.05 ± 0.19
Young's modulus/MPa	4.08 ± 0.21	3.91 ± 0.09

ate hand pressure, indicating rubber-like behavior. Conversion of hydroxyl groups to PU was estimated to exceed 95% based on the disappearance of monomer signals in the ^1H NMR spectrum and concomitant appearance of the respective methylene ester signals (4.28 ppm, Figures S7 and S8). Due to the compositional heterogeneity of BG-diol, the degree of polymerization cannot be precisely calculated, but the average number-average molecular mass (M_n) and weight-average molecular mass (M_w) were determined by GPC and are reported in Table 1. Proton NMR and IR spectroscopy were used to assess the structure of **BG-PU** and **OLA-PU**. The collected ^1H NMR spectra revealed expected chemical shifts in the designed PUs. Characteristic stretches found in the collected IR spectra, corresponding to the urethane linkage, are observed at 1705 (C = O stretch), 3313 (N–H stretch), and 1527 (N − H bend) cm^{-1}, respectively, for both **BG-PU** and **OLA-PU** (full spectra provided in Figures S7–S10).

The molecular weight distributions for **BG-PU** and **OLA-PU** were analyzed by gel permeation chromatography (GPC) using THF as the solvent and polystyrene (PS) standards for calibration. The results are summarized in Table 1 (GPC traces are provided in Figures S11 and S12).

The data indicate that **BG-PU** exhibits molecular weight characteristics similar to **OLA-PU**, with only a modest reduction in

Figure 3. Representative dog bones prepared for mechanical testing. **BG-PU** dogbone on the left and **OLA-PU** dog bone on the right. Dog bones were prepared by solution casting with DMF, dried at 50 °C for 24 h, and then dried in a vacuum oven at 50 °C for 6 h.

M_w and M_n values. The dispersity ($Đ$) for **BG-PU** remains within a narrow range (1.42), somewhat lower than the value of 2.00 for an ideal step-growth polymerization, but similar to the value for the **OLA-PU** (1.46). Despite originating from an unrefined feedstock (brown grease), the resulting polymer exhibits comparable molecular weight distribution, glass transition temperature, and thermal decomposition onset to the material derived from purified oleic acid.

The thermal properties of **BG-PU** and **OLA-PU** were analyzed by thermogravimetric analysis and differential scanning calorimetry (TGA and DSC curves are provided in Figures S13–S18). Results shown in Table 1 highlight the similarity between **BG-PU** and **OLA-PU**, with 5% mass loss for both polymers observed at 270 °C and 267 °C, respectively. Glass transition temperatures of both polymers are also reported in a similar range with a T_g of 24 °C and 15 °C for **BG-PU** and **OLA-PU**, respectively.

Mechanical testing of **BG-PU** and **OLA-PU** was performed on solution-cast dog bone-shaped test items (Figure 3), revealing that the two materials have simile elastomeric properties (Table 1). **BG-PU** exhibited an elongation at break of 59.9% ± 0.60%, an ultimate tensile strength of 1.05 ± 0.019 MPa, and a Young's modulus of 3.91 ± 0.076 MPa (Figure S19). **OLA-PU** showed slightly higher values, with an elongation at break of 62.9% ± 0.24%, an ultimate tensile strength of 1.35 ± 0.021 MPa, and a Young's modulus of 4.08 ± 0.21 MPa (Figure S20). Despite the inherent variability in brown grease, the mechanical performance of **BG-PU** closely matches that of the PU derived from pure oleic acid.

Other PUs prepared from bio-based feedstocks include a report of copolymerizing undecylenic acid and MDI.[38] The undecylenic acid-derived PU was reported to have an M_n and M_w of 50.9 and 96.3 kDa, respectively, with a T_g of 20 °C, a $T_{d,\,5\%}$ of 269 °C, an elongation at break of 320% and an ultimate tensile strength of approximately 12.5 MPa.[38] In comparison to **BG-PU**, the undecylenic acid-derived PU has similar thermal properties, but a higher molecular weight and concomitantly higher mechanical strength. A similar trend is also observed when comparing **BG-PU** to a triolein-derived PU, with a reported elongation at break of 136% and ultimate tensile strength of 7.9 MPa.[40] Further differences in mechanical properties are observed when comparing **BG-PU** to commercial-grade PUs, such as TPU 95A, a thermoplastic PU with an elongation at break of 82.3%, an ultimate tensile strength of 6.4 MPa, and a Young's modulus of 56 MPa.[41] Future work will investigate a broader range of diisocyanates comonomers for polymerization with **BG-diol**, and possible pretreatment of brown grease to improve uniformity prior to diol monomer formation in an effort to improve molecular weights of resulting polymers.

3. Conclusion

This study demonstrates the feasibility of using brown grease, an abundant and underutilized waste lipid source, as a precursor for polyol monomer synthesis and subsequent PU production. By employing a two-step functionalization strategy—transesterification followed by thiol-ene click chemistry—brown grease-derived polyols (**BG-diol**) were synthesized with high efficiency and successfully polymerized with MDI to yield **BG-PU**. Comparative characterization of **BG-PU** and PU derived from pure oleic acid (**OLA-PU**) revealed similar molecular weight distributions, thermal properties, mechanical properties, and polymer structure, indicating that brown grease can serve as a viable alternative to high-purity fatty acid feedstocks.

The use of brown grease for PU synthesis presents both economic and environmental advantages. It provides a cost-effective alternative to plant oils, reducing reliance on agricultural resources while diverting waste from disposal. Furthermore, the mild, selective nature of the thiol-ene reaction enhances process efficiency and sustainability by minimizing energy input and byproduct formation. Despite efforts to employ high-yield steps and sustainable precursors, sustainability of the polymer preparation is compromised by the need to use an of excess reagents in the esterification step, leading to a high E factor (∼74) for the preparation of **BG-PU**. This highlights opportunities for process optimization, specifically with reagent stoichiometry and purification techniques. Nonetheless, this study supports development of a broader effort in waste lipid valorization strategies for polymer applications. Future work will assess the scalability and broader applicability of brown grease as a precursor to a wider range of PUs, and mechanical performance of these series of materials will be evaluated.

4. Experimental Section

4.1. Materials and Methods

Reagents were used as received from Millipore Sigma, Acros Organics, Polymer Source Inc., and Thermo Fisher Scientific. Suppliers for brown grease omitted to avoid endorsement or bias. Proton NMR spectra were obtained on a Bruker NEO-300 operating at 300 MHz at 20 °C–23 °C. Chemical shifts (δ) are reported in parts per million (ppm). Spectra data was processed with SpinWorks 4.2.11 software and referenced to residual solvent peak (^1H, $CDCl_3$, 7.26 ppm). Multiplicity is reported as s, singlet; d, doublet; and m, multiplet. Fourier transform infrared spectra were collected on Shimadzu IR Affinity-1S with an ATR attachment operating over 400–4000 cm^{-1} at 20 °C–23 °C. IR peaks were reported in cm^{-1}, with indicated relative intensity w (weak, 67%–100% T). Elemental analyses were obtained from Atlantic Microlab, Inc. Gel permeation chromatography (GPC) was performed on a Shimadzu GPC with a Phenogel 5 u 10E4A gel column and RID 10A detector. Tetrahydrofuran (>99.8%) was used as the eluent with a flow rate of 1 mL min^{-1}, and polystyrene was used as the standard to calibrate the GPC instrument from 290000 to 7215 molecular weight. Data was acquired on LabSolutions GPC software. Differential scanning calorimetry (DSC) was performed, and data was collected on a Mettler Toledo DSC 3 STARe System over the range of −60 °C to 140 °C with a heating rate of 10 °C min^{-1} under a flow of N_2 at a rate of 200 mL min^{-1}. Samples run through the DSC were measured over three heat–cool cycles. Thermogravimetric analysis (TGA) was performed, and data was collected on a TA SDT Q600 instrument over the range of 25 °C–800 °C, with a heating rate of 10 °C min^{-1} under a flow of N_2 at a rate of 20 mL min^{-1}.

4.2. Synthesis

Allyl oleate, **OLA-diol** and **OLA-PU** were prepared according to a modified literature procedure.[38]

Allyl brown grease (**allyl-BG**). A 100 mL round-bottom flask equipped with a stir bar and condenser was charged with allyl alcohol (>98.5%, 30.0 g, 517 mmol, excess), brown grease (14.7 g, mmol cannot be determined due to the complexity of brown grease), and *p*-toluenesulfonic acid monohydrate (99%, 2.46 g, 12.9 mmol, ~2.5 mol% with respect to allyl alcohol) sequentially. The reaction mixture was heated to 120 °C in an oil bath for 16 h and cooled to room temperature afterward. The reaction mixture was then dissolved in diethyl ether (99%, 60 mL), followed by aqueous extraction with saturated sodium bicarbonate solution (2 × 60 mL) and water (2 × 60 mL) to remove the excess allyl alcohol. The organic layer was collected, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude liquid was dissolved in ethyl acetate (99.5%, 50 mL), and the solution was vacuumed filtered through a 3 cm silica plug in a 10 cm (diameter) Büchner funnel and rinsed with ethyl acetate (99.5%, 300 mL) to remove unreacted triglycerides and fatty acids. The organic layer was collected and concentrated under reduced pressure to obtain the desired product as a brown liquid (13.8 g, yield cannot be determined due to the complexity of brown grease). Proton NMR [300 MHz, $CDCl_3$, δ (ppm)]: 5.93 (m, $-CH=C$, 1H), 5.34 (m, $-CH=CH-$, 2H), 5.23 (m, $C=CH_2$, 2H), 4.58 (d, $-OCH_2$, 2H), 2.35 (t, $-CH_2-CO-$, 2H), 2.06 (m, $-CH_2-C=C-CH_2-$, 4H), 1.65 (m, $-CH_2-CCOO$, 2H), 1.32 (m, $-CH_2-$, 22H), 0.88 (m, $-CH_3$, 3H). Elemental analysis [(elements present: C, H, N, O), (elements analyzed for: C, H, N)]: calculated C, 78.45; H, 11.60; N, 0–3.00. Found C, 77.44; H, 11.78; N, 0.16. (Atlantic Microlab, Inc.).

4.3. Preparation and Characterization of Brown Grease Diol (BG-Diol) and Brown Grease-Derived Polyurethane (BG-PU)

This material was prepared according to a modified literature procedure.[38]

Brown grease diol (**BG-diol**). A 20 mL scintillation vial equipped with a stir bar was charged with **allyl-BG** (3.36 g, mmol cannot be determined due to the complexity of brown grease), 2-mercaptoethanol (>98%, 7.37 g, 94.5 mmol, excess), and 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%, 108 mg, 0.421 mmol) sequentially. The mixture was agitated, and acetonitrile was added (99.8%, 0.157 g, 3.82 mmol) to dissolve the DMPA. The reaction was carried out at 22 °C by irradiation with the Photoreactor M2 ($\lambda = 365$ nm, 100% LED, 100 rpm (stir), 6810 rpm (fan), 30 s post-cool) for 24 h. The reaction mixture was then dissolved in diethyl ether (99%, 40 mL), followed by aqueous extraction with saturated sodium bicarbonate (4 × 40 mL) and water (2 × 40 mL) to remove excess 2-mercaptoethanol. The organic layer was collected, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford the desired product as a yellow oil (3.40 g, 90.7% yield based on theoretical conversion of all olefins). Proton NMR [300 MHz, $CDCl_3$, δ (ppm)]: 4.16 (t, $-CH_2-OCO-$, 2H, 3.71 (m, $-CH_2-O-$, 4H), 2.73 (m, $-CH_2-S-$, 4H), 2.59 (m, $-CH-S-$, $-CH_2-SCCO-$, 3H), 2.29 (m, $-CH_2-COO-$, 2H), 1.92 ($-OCOC-CH_2-CS-$, 2H), 1.25 (m, $-CH_2-$, 30H), 0.89 (m, $-CH_3$, 3H). Elemental analysis [(elements present: C, H, N, O, S), (elements analyzed for: C, H, N, S)]: calculated C, 62.72; H, 10.53; N, 0–3.00; S, 13.39. Found C, 63.39; H, 10.64; N, 0; S, 12.39. (Atlantic Microlab Inc.).

Brown grease–derived polyurethane (**BG-PU**). A 100 mL round bottom flask was equipped with a stir bar and charged with dimethylformamide (99.8%, 11.4 g, 156 mmol), **BG-Diol** (3.29 g, mmol cannot be determined due to the complexity of brown grease), 4,4′-Methylene diphenyl diisocyanate (MDI, 98%, 1.73 g, 6.91 mmol), and tin (II) 2-ethylhexanoate (92.5%–100%, 84.3 mg, 0.208 mmol) sequentially. The reaction mixture was heated to 50 °C in an oil bath for 24 h and cooled to room temperature afterward. The reaction mixture was then poured into diethyl ether (99%, 200 mL) to precipitate out the polymer as a crude solid. The crude solid was collected, dissolved in a minimum amount of chloroform (99.8%, 15 mL), and reprecipitated into diethyl ether (99%, 200 mL) for purification. The purified material was dried under vacuum at 70 °C for 24 h and collected to afford the desired product as a brown solid (0.614 g, yield cannot be determined due to the complexity of brown grease). Proton NMR [300 MHz, $CDCl_3$, δ (ppm)]: 7.26, 7.07 (m, $-N-C_6H_4-$, 8H); 4.28, 4.16 (m, $OCO-CH_2-$, 4H); 3.86 (m, $Ph-CH_2-Ph$, 2H); 2.77– (m, $COCO-CH_2-S$, 2H); 2.62 (m, $OCOCC-CH_2-S$, 2H); 2.29 (m, $OC-CH_2-$, 2H); 1.85 ($SC-CH_2-COCO$, 2H), 1.37 (m, $-CH_2-$, 22H); 0.85 (m, $-CH_3$, 3H). Elemental analysis [(elements present: C, H, N, O, S), (elements analyzed for: C, H, N, S)]: Calculated C, 65.72; H, 8.55; N, 3.83; S, 8.77. Found C, 64.64; H, 7.77; N, 4.25; S, 8.40. (Atlantic Microlab Inc.) IR (cm^{-1}); 3313 (w, N-H stretch), 2920 (w, C–H stretch), 1705 (w, $C=O$ stretch), 1527 (w, $N-H$ stretch), 1303 (w, C–N stretch).

Author Contributions

The author primarily responsible for particular CRediT roles are provided here. **Y.B.K.**: Data curation; formal analysis; investigation; validation; writing—review and editing. **A.G.T.**: Resources. **A.D.S.**: Funding acquisition; resources; writing—review and editing. **R.C.S.**: Conceptualization; methodology; funding acquisition; resources; supervision; writing—review and editing.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Low-value fats · Step-growth polymerization · Thiol-ene reaction · Transesterifications · Upcycling

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