Glycerol ketals as building blocks for a new class of biobased (meth)acrylate polymers

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Abstract

Here we present an approach for developing the next generation of bio(meth)acrylates using glycerol ketals as a platform for property differentiation. Crude glycerol, a biodiesel byproduct, and ketones, derived from biomass valorization, are the building blocks for these polymeric materials. Biobased materials are witnessing a prominent boom in research and commercialization due to increased awareness about the carbon footprint and depletion of petroleum resources. Biodiesel and biopolymers are major linchpins to improve sustainable energy and material needs of the world in the coming years. Glycerol ketal (meth)acrylate monomers synthesized by the reaction of glycerol and various ketones consist 65-74 wt.% bioderived content. Glycerol ketals from different ketones used in our study (acetone, cyclopentanone and butanone) are the pendant groups on the (meth)acrylate polymer backbone. We studied the effect of various pendant side-chain ketal groups on the thermal and rheological properties of these polymers. The methacrylate polymers had a higher glass transition temperature (T_g) (8–40 ° C) while the acrylate derivatives had much lower T_g between -11 °C to 2 °C. The side chain group on these polymers offers us a robust knob to tune the thermal properties (e.g. T_g) and rheological properties (e.g. modulus and entanglement behaviour) for varied applications such as hard block polymers and adhesives.

Keywords

Biopolymers, curde glycerol, glycerol ketals, (meth)acrylate polymers

Introduction

With more vehicles on the road every year, the depletion of fossil fuel resources and the continued release of greenhouse gases, there is an ever-expanding need for renewable fuels. Biodiesel has emerged as a potential substitute for diesel fuel as it is believed to be carbon-neutral and does not require modification of current diesel engines. In 2018, the National Diesel Board Report cited a biodiesel production goal of 4 billion gallons for the US by 2022.[1] Production of biodiesel generates about 10 wt% glycerol as a coproduct, implying about 400 million gallons of glycerol that floods the market every year. Thus to make the biodiesel production more sustainable researchers need to find high value applications of glycerol.[2,3]

Markets for glycerol-based polymers could potentially offer the right balance of volume and value for this purpose. In the past decade, researchers have extolled the virtues of glycerol based polymers for biomedical and pharmaceutical applications.[4,5] Various polymers such as polyols,[6] hyperbranched polyglycerol dendrimers,[7–9] and polyglycerol carbonates[10,11] have been considered for drug delivery and implants. However, impurities in "crude" glycerol from biodiesel production process such as methanol, fatty acid methyl esters, soap, and water make it unsuitable for personal care and medical applications. Almost all crude glycerine is either burnt as fuel in biodiesel plants or further refined and processed. The purification process is

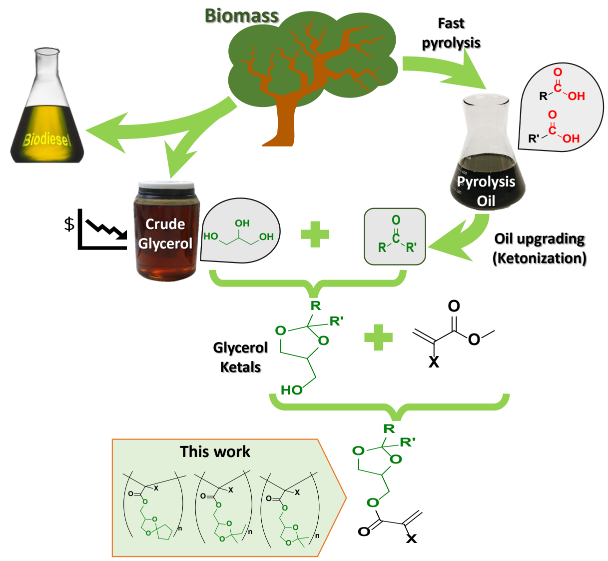

Figure 1: Glycerol ketal polymers from biobased building blocks

energy intensive and further adds to the economic stress of biodiesel production. In 2019, the price of crude glycerol plummeted to \$170/t while purified glycerol was traded at an average of \$895/ton.[12] Significant attention has been drawn to synthesizing value added chemicals from crude glycerol via different catalytic (oxidation, dehydration, dehydrogenation etc.) or biological (aerobic, anaerobic) pathways.[13–18]

Recent efforts to valorize the glycerol surplus include its conversion to cyclic acetals and ketals for use as fuel additives,[19–21] flavors, surfactants,[22] and low toxicity biobased solvents.[23] Glycerol ketals are synthesized by a straightforward condensation reaction between glycerol and respective ketone. Homogeneous and heterogeneous catalysis,[24] microwave-assisted solvent- and catalyst free-reactions[25] have been reported to improve the selectivity and conversions of these glycerol ketals. Our interest was drawn to glycerol ketals due to their increased potential for commercialization from the availability of ketones derived directly from biomass. Bio-oil derived from fast pyrolysis or aqueous phase hydrolysis of biomass is a complex mixture of furanics, phenols and carboxylic acid groups. The neutralization of these acid groups is a primary upgrading step to generate value-added chemicals.[26] Ketonization reaction converts two molecules of acid (or ester) into a ketone, CO_2 and water.[27] Depending on the feed source and catalysts, various ketones such as acetone, 2-butanone, nonanone, cyclohexanone, cyclopentanone can be synthesized with high yields.[28–31] The hydroxyl groups on these ketals become useful functional handles for imparting polymerizing groups such as vinyl, acrylic, and methacrylics. Acrylates, methacrylates and their corresponding polymers are important classes of materials that have been studied widely.[32–34] Over 10 million metric tons of a variety of (meth)acrylate polymers are consumed globally each year.[35,36] Through backbone and pendant group choices, these crucial polymers adopt diverse chemical, thermodynamic, and thermomechanical properties serving wide-ranging markets including paints, plastics, adhesives, fabrics, additives, optics, biomedical/biomaterials, and electronics. Several advances towards the commercialisation of biobased acrylic and methacrylic acid, key precursors, have been reported in recent years.[37–40] However, there is a need for new biobased pendant groups to complete the transformation of the (meth)acrylate industry without compromising the utility of the materials it provides. Recently, we reported glycerol as a useful biobased pendant group that yields water-soluble branched chain elastomers suitable for wood composite adhesives.[41] Glycerol ketals provide a means to extend the utility of glycerol as a pendant group by diversifying the range of accessible bio(meth)acrylates to compete with the incumbent petrochemicals.

Previous work with glycerol ketal acrylic polymers have only been focused on polymerization kinetics. Socha et al. synthesized polymers with methyl methacrylate derivates of 2-isopropyl-4-methyl-1,3 dioxane and 2-propenyl-1,3 dioxane through ring opening polymerization and outlined the conversion rates.[42] P.D. Pham et al. synthesized oligomers by free-radical chain transfer polymerization of solketal acrylate monomer using 2-mercaptoethanol as chain transfer agent. They reported oligomers with 4.7 kDa molecular weight and dispersity of Đ = 1.27.[43] These investigations, however, are silent on the properties of these polymers. Given the rich variety of acyl-functional biorenewables available, glycerol ketal (meth)acrylate building blocks are a platform for a new generation of sustainable polymeric materials. A pertinent step in realizing the potential of these polymers is the development of structure-property relationships that will enable us to design materials for various applications based on chemical identity and resultant thermomechanical properties.

The aim of this study is to report the potential for property modification of a family of (meth)acrylate polymers through biobased side chain groups. The ketal side chain groups on these polymers offer a possibility for low cost raw material, crude glycerol utilization for high volume polymeric material applications (Fig. 1). In this work we introduce a series of linear low dispersity RAFT-based homopolymers from glycerol ketal (meth)acrylate monomers constructed via lipase enzyme catalyzed enzymatic transesterification. Rheology and thermal properties of these were studied to assess the effect of various pendant chain groups.

Experimental Section

Chemicals

2-cyanopropan-2-yl ethyl carbonotrithioate (CYCART) used as the chain transfer agent (CTA) for RAFT homopolymers and was synthesized as described in the ESI based on known methods.[44,45] S,S-dibenzyl trithiocarbonate (DBTTC, Sigma-Aldrich) was the CTA for the symmetric ABA triblock copolymer. Cyclohexyl/butyl ketals and (meth)acrylate derivatives thereof were synthesized in-house. Solketal is commercially available and was used for the synthesis of solketal (meth)acrylates. Glycerol (99.7% w/w) was purchased from VWR; crude glycerol was obtained through REG Inc. in Ames, IA. p-toluenesulfonic acid (TSA), methyl methacrylate (MMA, $\geq$ 98%), toluene (Tol, $\geq$ 99.5%), tetrahydrofuran (THF, $\geq$ 99.9%), methyl ethyl ketone (MEK, $\geq$ 99%), Hexanes were acquired from Fisher-Scientific. DL-1,2-isopropylideneglycerol (commonly known as solketal) (Sol, $\geq$ 97%) was purchased from Sigma-Aldrich. The enzyme lipase Acrylic resin from *Candida antarctica* lipase (commonly known as Novozyme 435) was purchased from Sigma Aldrich for transesterification. Isobornyl acrylate (IBA, Sigma-Aldrich) was passed over inhibitor removers prior to polymerization. All chemicals were used as received.

Glycerol Ketalization procedure

The reaction was carried out in a 3-neck 1000mL round-bottom flask with a Dean-Stark tube and condenser. Glycerol (1 mol) and adequate ketone (3 mol) was added with TSA (1.5% w/w of glycerol) and toluene. The reaction scheme is depicted in Fig. 2. The reaction was mechanically stirred and heated under reflux overnight. The water generated was collected in the dean stark apparatus through toluene-water azeotrope. The reaction mixture was washed with water (2×150 mL) and brine (1×150 mL) and distilled under vacuum. The purity of the premonomer was ascertained through ^{1}H-NMR and GC-MS.

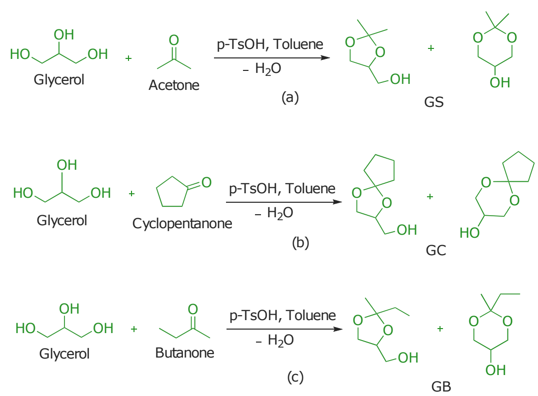

Figure 2: Premonomer synthesis by the reaction of glycerol and ketone with p-toluene sulfonic acid catalyst and toluene as reflux solvent in dean stark apparatus

Enzymatic Transesterification: Ketal (meth)acrylate Derivative

The enzymatic transesterification reaction was carried out using premonomer, excess methy methacrylate (MMA)/methyl acrylate (MA) with lipase enzymes and molecular seives at 40 ° C using mechanical agitator for 24 h. The reaction scheme is shown in Fig. 3. The extent of reaction was determined using 1H-NMR. The unreacted MMA/MA was removed by rotary evaporation and the monomer was purified through flash chromatography using hexanes and ethyl acetate. The purity of the monomer was ascertained through GC-MS and the monomer was put in vacuo for 24 h.

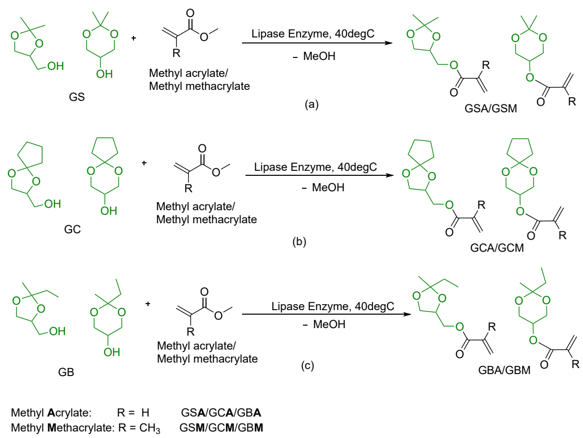

Figure 3: Monomer synthesis by the reaction of glycerol ketal with methyl acrylate/methyl methacrylate with Lipase enzyme as the catalyst at 40 ° C (a). Solketal (GS) (b). Glycerol-cyclopentanone ketal (GC) (c). Glycerol-butanone ketal (GB)

RAFT Polymerization

AIBN and CTA were added to the monomer in a vial and toluene was added as solvent. The reaction mixture was purged with argon for at least 20 minutes and the polymerization reaction was carried out at 80° C for 4 hrs. The polymer was precipitated and purified by three cycles of dissolving-precipitating using THF and hexanes and dried under vacuum for 24 hours. RAFT polymerisation recipes are provided for each polymer specimen in the ESI. Poly(isobornyl acrylate-*block*-solketal acrylate-*block*-isobornyl acrylate) (IBA-GSA-IBA) was produced using a macromonomer strategy. First, poly(isobonyl acrylate) macromonomer was formed by combining IBA (18 g, 86 mmol), DBTTC (0.17 g, 600 μmol), AIBN (19.7 mg, 120 μmol) and toluene (18 g, 0.20 mol) in a 250 mL round-bottom flask. The mixture was purged for 30 min with argon, and then polymerisation was conducted at 80 °C for 8 h. Macromonomer was precipitated from methanol three times and dried. Macromonomer (14 g, 1.17 mmol), SA (200 g, 1.08 mol), AIBN (0.14 g, 0.85 mmol) and toluene (214 g, 2.32 mol) were sealed and purged under argon for 30 mins in a 1 L round-bottom flask and polymerised at 90 °C for 8 h, precipitated from methanol three times, and dried.

Material Characterization

^{1}H-NMR were recorded on a Varian-400 MHz spectrometer. Chemical shifts were reported in ppm relative to $CDCl_3$ at 7.27ppm. GC-MS characterization was conducted on an Agilent 6890 GC coupled to an Agilent 5975C MS detector using an Agilent DB-1 column. SEC system used was a Waters Aquity UPLC system run in THF as eluent with a flow rate 0.8 mL/min at 50 °C column temperature. It is equipped with a refractive index detector and a uv-vis detector. This system contains 4 columns Acquity APC XT450, 2×XT200, and XT45 in series. M_n, M_w and dispersity (Đ) of the polymers were determined through integrating the RI detector signal against a polystyrene calibration curve. DSC was used to study the thermal properties of the polymers on TA Instrument Q2000. The samples were prepared in Aluminium Hermetic T-zero pans.The samples were heated from -60° C to 50° C in nitrogen atmosphere at a heating/cooling rate of 10° C/ minute and an isothermal equilibration was maintained for 1 min at the initial and final temperature. The data were analysed in the second heating cycle. TA instruments ARES G2 was used to study the rheological properties of the polymer using 8mm parallel plate. The frequency sweeps tests were carried out at different temperatures from -10° C to 100° C at the strain % from the LVE from $\omega = 0.1$ rad/sec to 100 rad/sec. Time Temperature Superposition (TTS) through Trios Software wizard was used to generate master curves at reference temperature and the shift factors were regressed through the Williams-Landel-Ferry (WLF) equation. DMA measurements were also performed on the Ares G2. Temperature ramp experiments were performed in a temperature range of -50 to 60 °C and a heating rate of 5 °C/min with a fixed frequency of 1 Hz. The strain imposed was in the linear regime.Thermal stability of the polymers was studied using TA Instruments Thermogravimetric Analyser TGA 5500. 3-5 mg samples were analyzed with a heating rate 20 °C/minute in nitrogen atmosphere.

The performance of an exemplary IBA-GSA-ISA adhesive formulation was evaluated with 180^{o} peel testing on a glass substrate using an I-MASS SP-2100 slip-peel tester at a peel rate of 30.5 cm/min.

Results and discussion

We synthesized GC and GB ketal premonomers via the TSA-catalysed reaction of glycerol with cyclopentanone or butanone in a Dean-Stark apparatus with toluene reflux as shown by reaction scheme in Fig. 2. Solketal (GS) was purchased but can be synthesised by a similar reaction between glycerol and acetone.[46,47] We obtained >80% yield; GC and GB structures were confirmed with ^{1}H-NMR as shown ESI Fig. S1–S2. The reaction was conducted with excess glycerol which was removed by a series of benign solvent ethyl acetate/water liquid-liquid extractions (LLE). We repeated the GC synthesis with crude glycerol and were able to achieve the same yield and purity. The impurities present in crude glycerol did not interfere with the ketal synthesis or purification were removed in the subsequent workup (ESI Fig. S9). GC-MS of the GC and GB after LLE indicated about 80% purity with glycerol as the primary contaminant. We obtain a mixture of isomeric 5- and 6- membered cyclic ketals by the reaction of primary and/or secondary hydroxyl groups on glycerol with the respective ketone. Though GC-MS results indicate that the 5-membered ring is predominant.(ESI Fig. S10-S12) The mixture of both isomers was used for transesterification reaction. When carried forward through (meth)acrylation, the resultant monomer is a mixture of monofunctional ketal (meth)acrylate and multi-substituted glycerol (meth)acrylates. As we reported previously, under RAFT polymerisation these multifunctional monomers form branched chain polymers with very high molecular weight ($\gg$ 100 kDa).[41] While these polymers represent the most efficient conversion process, here our motivation is to characterise and understand the basic properties of the linear (meth)acrylate glycerol ketal polymers. Hence we further vacuum distilled the premonomer to reach 99.5% purity per GC-MS prior to solvent-free enzymatic transesterification with methyl (meth)acrylate at 40 °C using 5Å molecular sieves to remove any methanol generated as depicted by reaction scheme in Fig. 3. Enzymatic transesterification is less energy intensive and generates lower waste content than chemical catalysis which is why biocatalysts are gaining attention as an alternative process to chemical catalysis for sustainable and greener biodiesel production.[48–50] Excess methyl (meth)acrylate was removed by rotary evaporation and flash chromatography (FC) was performed to yield a clear viscous liquid monomer. The room temperature viscosity of the monomers is around 4-5.5 centipoise. NMR spectra for the monomers (GCA, GCM, GSA, GSM, GBA, and GBM) appear in ESI Figs. S3–S8. Enzymatic transesterification results in high yields (70-80%) at lower reaction temperatures (25-40 °C), which reduces the possibility for any in-situ polymerization of the monomer, i.e. no inhibitor was needed during monomer synthesis. Glycerol ketal (meth)acrylate monomers consist of 65-74 wt% bioderived content. We then applied RAFT polymerisation to produce linear polymers with molecular weights ranging from 10 – 40 kDa and low Đ. The pendant groups did not significantly impact the polymerisation kinetics, while polyacrylate polymerisation was far more rapid than polymethacrylate. RAFT recipes are provided in Table S1. Molecular characteristics of the polymers are provided in Table 1.

Having synthesised a range of molecular weights for all polymers we began with studying their structure-property relationships, the results of which are summarised in Table 1. The acrylate derivative polymers (-11 – 5 °C) had much lower T_g as compared to the methacrylate polymers (20 – 50 °C) which is expected due to less steric hindrance of the methyl group on the backbone carbon chain and has been seen in a variety of other works. However, the pendant group on the polymer chains also affect the T_g due to the bulkiness of side groups restricting chain mobility.[51] T_g for acrylate derivatives of cyclopentyl ketal side group (GCA) samples are about 10 °C higher than T_g for dimethyl ketal side group (GSA) for similar molecular weights. The rigid cyclopentane group restricts chain movement and increases the T_g for GCA polymers. But comparing similar molecular weight samples of

Table 1: Gel Permeation Chromatography (GPC), Differential Scanning Calorimetry (DSC) and Rheology results for polymers

Sample Code	T_g, °C DSC	T_g, °C DMA	G_x, MPa	log ω_x	M_n, kDa	$Đ$
GSM1	50.9	72.8	88.12	5.1	17.06	1.18
GSM2	53.7	73.1	98.38	4.9	25.35	1.23
GSM3	47.0	73.4	79.48	4.9	29.81	1.28
GCM1	38.4	69.5	86.50	5.3	17.39	1.15
GCM2	47.2	70.9	93.71	5.1	32.76	1.29
GCM3	52.8	72.0	96.40	5.3	37.25	1.35
GBM1	23.8	55.3	70.66	6.3	16.04	1.26
GBM2	20.8	56.4	49.00	6.3	20.81	1.43
GBM3	34.8	61.7	55.24	5.9	34.12	2.16
GSA1	-11.2	15.2	9.28	5.3	13.9	1.19
GSA2	-3.4	16.0	83.86	6.2	18.12	1.35
GSA3	-5.9	17.3	166.74	6.2	20.73	1.59
GCA1	-1.4	15.7	166.35	5.6	10.58	1.14
GCA2	5.8	18.4	164.84	5.4	17.04	1.18
GCA3	5.9	18.9	185.36	5.2	22.49	1.21
GBA1	-6.5	1.7	77.20	6.4	10.39	1.16
GBA2	-6.9	0.6	80.64	6.4	16.46	1.21
GBA3	-5.8	0.8	157.97	6.3	21.1	1.27

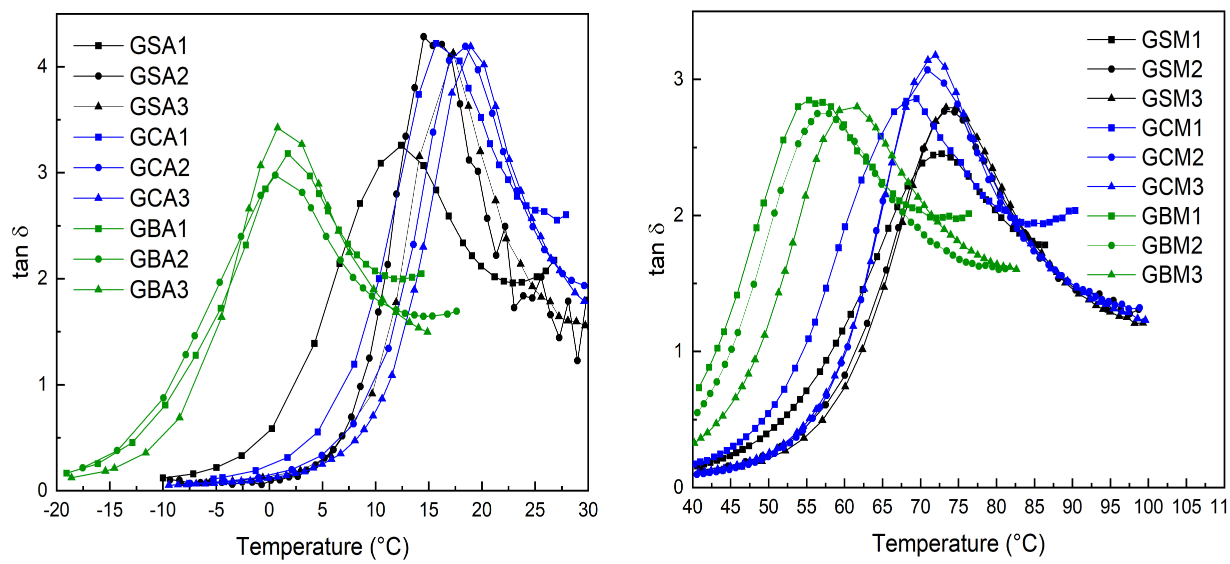

Figure 4: DMA results of glycerol ketal acrylate (left) and glycerol ketal methacrylate polymers (right)

methacrylate derivatives, T_g for GSM1 is higher than GCM1 while GSM3 and GCM2 manifest comparable T_g. The methyl group on the backbone provides higher steric hinderance to the bulky cyclopentyl group increasing free volume slightly for GCM samples while the smaller dimethyl groups ensure better packing in GSM polymers. This provides an evidence that a balance between the chain restriction due to rigid side groups and increase in free volume due to length or steric hinderace account for the resultant T_g of these materials. The longer flexible pendant alkyl chains in GBM/GBA, on the other hand, increase the free volume per chain, reduce the entanglement density and makes it easier for the chains to slide over each other resulting in the lowest values of T_g. When a polymer is heated through T_g, the chain segment motions increase dramatically and thus the local relaxation times of the polymer are evident to the mechanical T_g observed in DMA (Table 1). The location of maxima in $\tan\delta$ in temperature ramp (5 °C /min at 1 Hz) DMA experiments is reported as the T_g in Fig. 4 which is evident of damping characteristics of polymer chains due to decrease in the strength (G') and increase in polymer chain mobility (G"). In general, T_g values and trends obtained through DSC and DMA concur well with each other. Therefore, various pendant side chain groups (from different ketones) significantly influences the chain mobility and offering a means to tailor the T_g for diverse end-use applications. Other ketone groups would help us elucidate better the effects of rigidity, length and functional groups of pendant chains on thermomechanical properties of these materials. In future studies, additional ketones obtained in high yields from the pyrolysis of bio oil such as longer alkyl chain (hexanone, 5-nonanone)/cyclic compounds (methyl-cyclohexanone, 2-cyclopentenone) could be interesting to synthesise polymers with an even broader range of lower/higher T_g values.[28–31] Similar effects of the pendant chain groups on thermal and mechanical properties are observed in acrylate and methacrylate family of polymers which make them suitable for a wide range of applications. These polymers are ubiquitous and are used in several industries such automotive parts, adhesives and sealants, paints additives, plasticisers etc. For instance, methyl acrylate (T_g = 10 °C) is used in water based coatings and paint industry to provide water and sunlight resistance while ethyl acrylate (T_g = -24 °C) is primarily used in elastomers, textiles, leather products, and denture materials. Our monomer synthesis process and polymerisation kinetics are robust and suitable for any ketone groups derived from myriad biomass sources from aromatic to long alkyl chains. Consequently, we could develop a family of biobased (meth)acrylate polymers with a range of properties for numerous end uses.

We also studied the thermal stability of the polymers (GSA3, GCA3, GBA3, GSM3, GCM3, and GBM3) using TGA provided in ESI Fig. S13. As expected the glycerol ketal (meth) acrylates depict similar degradation properties as poly(methyl methacrylate) (PMMA) and poly(methacrylate) (PMA). GSA, GCA and GBA demonstrate single decomposition step at T $>$ 330 °C (20 °C/min ramp in dynamic TGA) as observed in PMA between 320-450 °C (15 °C/min ramp in TGA).[52] Malhotra et al. suggested thermal stability of polymers decreases as bulk size of the pendant group increases.[53] Glycerol (ketal) acrylates demonstrate similar behaviour where thermal stability follows the order GSA $>$ GCA $>$ GBA for all values of weight loss. Previous work suggests that the presence of α-H in PMA results in various inter and intramolecular transfer reactions during degradation evolving pyrolysis gaseous products such as methanol, CO_2, dimers and trimers.[54] However, several factors such as tacticity, side chain groups, structure of end groups through different synthesis methods greatly influence the thermal stability of PMMA polymers.[55] They typically degrade in a two step chain scission depolymerization reaction between 275-350 °C evolving quantitative yields of MMA monomer exclusively.[56] GSM and GCM demonstrate a similar 2 step decomposition reaction between 190-400 °C while GBM exhibits higher thermal stability with a single step decomposition between 270-400 °C. PMMA polymers are known to exhibit unusual influence of side chain groups on thermal stability. The competition between ester decomposition of the backbone chain and depolymerization reactions is highly impacted by the side chain groups on methyl methacrylate polymers. For instance, t-butyl methacrylate undergoes predominantly ester decomposition reactions[57] while n-butyl methacrylate endures depolymerization reaction evolving monomer in addition to ester decomposition to anhydride structures in residue.[58] Certain side chain ester groups such as methyl, n-butyl, isobutyl degrade through a single step while the other group of methacrylate polymers with t-butyl, isopropyl or $\alpha-$methylbenzyl ester side groups degrade through two reaction steps.[55] The asymmetric methyl-ethyl side chain groups on GBM polymers also seems to be influencing the degradation mechanism of the methacrylate backbone polymer resulting in higher thermal stability.

In addition to thermal properties, the viscoelastic properties of polymer specimens are affected from various pendant groups and are seminal for understanding spatial arrangement of macromolecules. We compared the TTS-generated master curves for polymers with similar molecular weights to understand the rheological behaviour in Fig. 5. The master curves use reference temperatures of T_{ref} = 100 °C for methacrylates and T_{ref} = 40 °C for acrylates, about 30 °C above the respective T_g values.

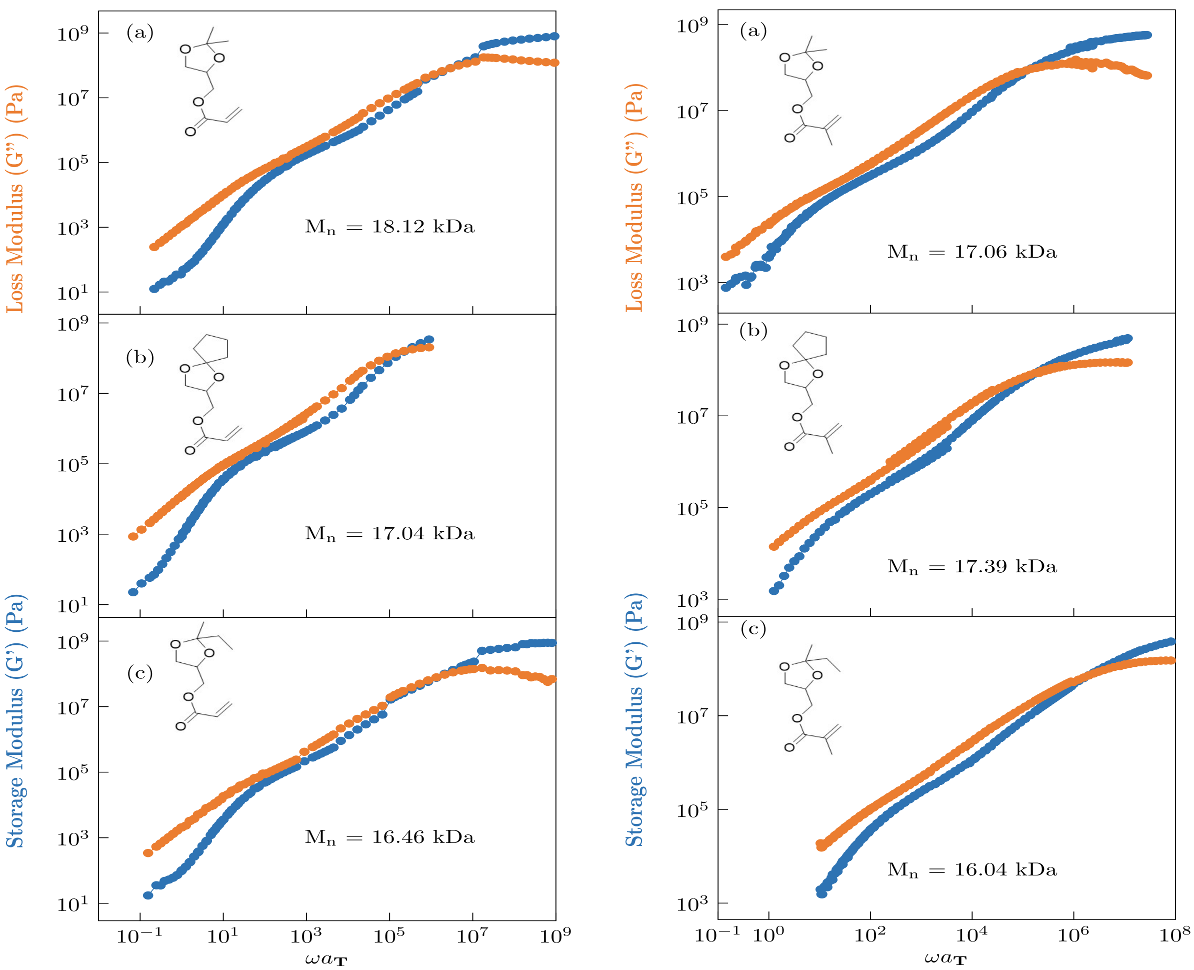

Figure 5: Time-temperature superposition (TTS) master curves for Glycerol Ketal Acrylate polymers of similar molecular weight at 40 °C **a**) GSA2 **b**) GCA2 **c**) GBA2 (Left) and Glycerol Ketal Methacrylate polymers at 100 °C **a**) GSM1 **b**) GCM1 **c**) GBM1 (Right)

At higher frequencies ($\omega \geq \omega_c$, where ω_c is the crossover frequency), G' for all polymer samples is of the order 10^9 Pa, *i.e.*, the material response is highly elastic ($G' \geq G''$). At the crossover point ($G' = G''$), the frequency of deformation (ω_c) is exactly equal to the relaxation time of the polymer. In other words, $\omega\tau = 1$ or the material is equally solid-like and liquid-like.[59] The relaxation time of the polymers is dependent on various factors such as molecular weight, temperature, side chain and backbone structure.

The results indicate ω_c decreases with molecular weight. At higher molecular weight the strand concentration increases, chains become more entangled and thus they find it difficult to leave the network which results in larger values of the relaxation time ($\omega = 1/\tau$).[60] The acrylic and methacrylic derivatives exhibit similar relaxation times (at $T = T_g + 30^o$C) and ω_c is similar for the different side chain groups. Hence the backbone configuration is the major contributor to the relaxation time of the polymers and has minimal effect due to the side chain group structures.

Beyond the transition zone the storage modulus G' theoretically plateaus and a minimum or dip is observed in the loss modulus G'' curve for uncrosslinked high molecular weight polymers in the entanglement dynamics regime. The individual chains become intertwined with one another and the internal degrees of freedom of the chain and its surroundings dictate the relaxation times. The plateau modulus G_N can be determined through various methods such as integrating over the G'' peak or the minimum peak value of loss tangent.[60] Trinkle et al. reported that the entanglement phenomenon can also be depicted as the Van gurp-Palmen (VgP) plot, which compares phase angle (δ) to complex modulus ($G*$); the value of $G*$ at minimum phase angle also approximately corresponds to G_N.[61] VgP plots for highest molecular weights of all samples are shown in Fig. 6. G_N was calculated from the VgP plot and the molecular weight between entanglements (M_e) was determined[59] for methacrylate and acrylate derivatives of these glycerol ketals given in Table 2.

$$M_e = \frac{\rho RT}{G_N} \tag{1}$$

Entanglement behaviour of polymer chains is affected by various conformational properties such as packing length ($p*$) and the characteristic ratio (C_∞). Packing length for a polymer chain is described as the volume occupied by a chain per unit mean square unperturbed end to end distance.[59] Flexible alkyl groups on the chain increase the average thickness of a single polymer chain which makes it harder for chains to entangle and hence increase the entanglement molecular weight. Thus, $M_{e,GBM} > M_{e,GSM} > M_{e,GCM}$. The methacrylate polymers exhibit higher molecular weight between entanglements than the acrylate polymers as the steric hinderance in the back bone due to the methyl group inhibits the chains to entangle and hence $M_{e,methacrylate} > M_{e,acrylate}$.

Table 2: Plateau modulus and molecular weight between entanglements

Sample	G_n (kPa)	M_e (kDa)
GSM	86.3	30.1
GCM	112.2	23.2
GBM	81.5	32
GSA	219	11.9
GCA	239.8	10.8
GBA	193.2	13.5

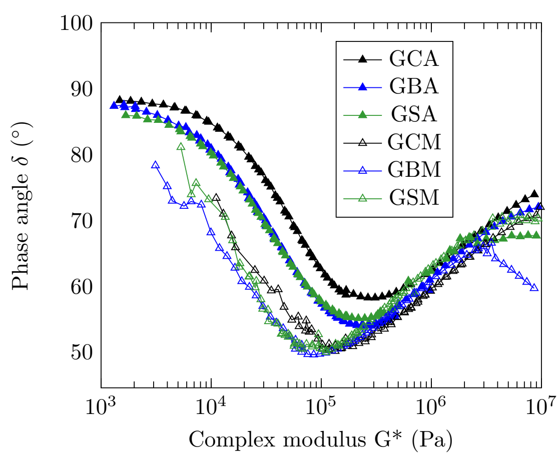

Figure 6: Van-Gurp-Palmen plot at 40 °C

Thermomechanical analysis of the PGK platform reveals a family of polymers with a wide range physical properties that can be tuned to develop useful materials from biomass.

With various pendant groups through choice of ketone, as block or random copolymers these materials can be explored for various applications as coatings, adhesives, hydrogels etc. Additionally, these glycerol ketal (meth) acrylates could also be explored to derive a wide array of properties with (meth)acrylate derivatives of other biosourced materials[62] such as terpenoid,[63,64] isosorbide,[65] and epoxidized soybean oil[66] to name a few. To illustrate this concept, we note that the polyacrylates show T_g values well below room temperature, are tacky under ambient conditions, and have low M_e values that signal robust elastic properties when prepared at moderate molecular weights. Pressure sensitive adhesives (PSAs) represent an exemplary application space whose material requirements aligns with these properties. Viable PSA formulations can first be screened through their rheological properties. PSAs require "tackiness" to facilitate physical bonding with the substrate as measured by the loss modulus G''; likewise, the storage modulus G' is a measure of the cohesive strength required to prevent debonding. G' and G'' values in the PSA performance window ($\omega \in [0.01, 100]$ rad/sec) provide accurate predictions of performance under normal use conditions.[67] At room temperature, GSA and GBA polymers demonstrate G'' values suitable for wetting, adhesion, and adhesive strength throughout the performance window (1–100 kPa).[68] However, these materials lack shear strength ($G' < G''$) and will creep on application of load and/or undergo cohesive failure on peel.

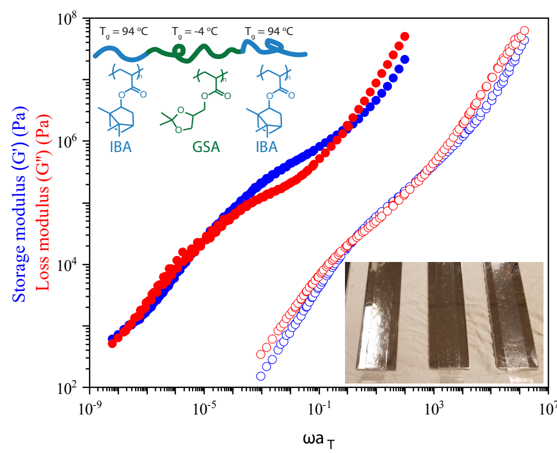

Figure 7: Time-temperature superposition master curve of a triblock copolymer using GSA as the soft block (solid) and its blend with the plasticizer (open) at T_{ref} = 25 °C

Such behavior is typical of an un-reinforced rubbery polymer; common strategies to enhance performance include increasing molecular weight/branching to promote entanglement dynamics in the performance window and/or introducing physical/chemical crosslinking. Random copolymers employed in PSAs often consist of branched structures and chemical crosslinks to increase gel content which provides the desired cohesion in PSAs.[63] However, for linear rubbery polymers, formulating PSAs by ABA triblock copolymer architectures is commonly used exemplified by the commercial SBS and SIS (styrene/butadiene or styrene/isoprene). ABA triblock copolymer comprises the hard block A with its T_g well above room temperature and the rubbery polymer B. ABAs constructed in this way are thermoplastic elastomers with sufficient mechanical strength and creep resistance. Here, both GSA and GBA are linear polymers which could serve as biobased replacements for the rubbery B segments. To demonstrate this potential, we prepared an exemplary ABA thermoplastic elastomer ($M_n = 109$ kDa) with GSA as the B block (88 wt %) and poly(isorbornyl acrylate) (IBA) as biobased A-block hard segments with $T_{g,IBA} = 94$ °C.[69,70] GPC traces (ESI Fig. S14) and molecular characteristics (Table S2) appear in the ESI. The master curve of this triblock copolymer appears in Fig. 7, revealing a rubbery plateau with $G_N \approx 10^5 Pa$ indicating the material strength enhancement. However, further formulating is required to adjust material properties resulting from the high G' ($10^5 - 10^7 Pa$) of GSA-triblock copolymer at the application frequency (0.01 - 100 rad/s). Typically PSA formulation includes polymer blend (20-50 wt%), tackifying resin (30-60 wt%), plasticizer (0-25 wt%) and stabilizer (0.1-2 wt%).[71] Since GSA itself shows enough tack, GSA-triblock copolymer PSA exhibit promising mechanical properties ($G'\&G" \in [10^3, 10^5]Pa$) at the application frequency by merely compounding with 30 wt% Benzoflex 2088 plasticizer (Fig. 7). The adhesive strength was tested by applying a 0.1 mm layer onto a 2.54 cm wide strip of Mylar® film. 180° peel-testing indicated an average peel force of 0.67 N/cm on a glass substrate; comparatively, 3M Scotch® Magic™ Tape shows a peel force of 1.5 N/cm under identical testing conditions. These triblock copolymers are thus promising candidates as PSA elastomers. Further studies are ongoing that outline a detailed characterization of these polymers for this application.

Conclusions

In this article, we have outlined the potential for glycerol ketals as biobased building blocks for polymeric materials. Glycerol by product from biodiesel production and various ketones obtained from ketonization of bio-oil offer a plethora of ketal groups that can be synthesized and used to develop novel biopolymers. Our study provides the framework for one of the ways through which the ketal groups provide a handle to modify properties of these polymers for different applications. We have succeeded in synthesizing the methacrylic and acrylic derivatives of these glycerol ketals via enzymatic transesterification and polymerizing them through RAFT. The results of this study give evidence of how the choice of (meth)acrylate backbone and pendant side chain groups can be used to influence the thermal and rheological properties of the polymers. The T_g for the acrylic derivatives was in the range -11 to 2 °C while the methacrylate derivatives had higher T_g in the range 8 to 40 °C. The stiff pendant side chain group such as cyclopentyl also restricts motion due to steric hinderance and results in higher T_g polymers as compared to flexible alkyl groups which reduce the glass transition temperature. The master curves for these polymers give evidence for longer chain relaxation time for methacrylate polymers as compared to the acrylate derivatives due to steric hindrances of the methyl group in the backbone. In addition, our preliminary results indicate that solketal acrylate polymers possess enough tack ($T_g < 0$ °C) such that their triblock copolymers with biobased isoboranyl acrylate as hard block are prospective candidate for pressure sensitive adhesive applications.

Conflicts of Interest

There are no conflicts of interest to declare.

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Supporting Information Available

The Supporting Information is available free of charge.

- CYCART RAFT chain transfer agent synthesis, ^{1}HNMR spectra of premonomers and monomers synthesized, ^{1}HNMR spectra of cyclopentanone ketal synthesis from crude glycerol, GC-MS spectra of glycerol ketal acrylates, TGA of (meth)acrylate glycerol ketal polymers, GPC traces of IBA macromonomer precurso and the IBA-GSA-IBA elastomer, RAFT polymerization recipes for all polymers, Characteristics of GSA containing triblock copolymers studied for PSA application.

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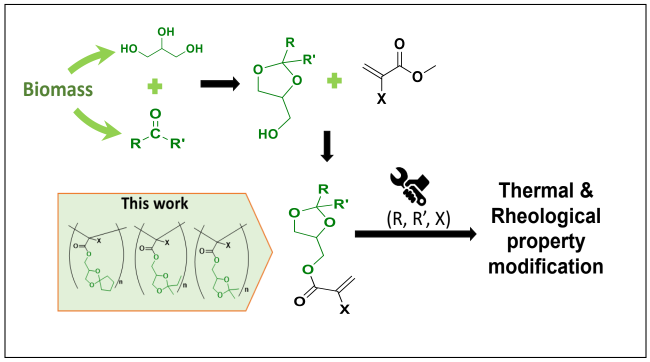
Graphical TOC Entry



Crude glycerol from biodiesel production and ketones from bio-oil ketonization process can be used to synthesize biobased glycerol ketals (meth)acrylate polymers. The choice of pendant groups from ketones can be used for property differentiation.