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Authors: Anjeza Beharaj, Iriny Ekladious, and Mark W Grinstaff

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Poly(Alkyl Glycidate Carbonate)s as Degradable Pressure Sensitive Adhesives

Anjeza Beharaj, Iriny Ekladious, and Mark W. Grinstaff*

Abstract: Polyacrylates are widely used in industry; however, their all aliphatic backbone leads to minimal degradability with challenges in recovery and recyclability. Insertion of CO_2 into the backbone, forming poly(carbonate) analogues of poly(acrylate)s provides an environmentally friendly and biocompatible alternative polymer. The synthesis of five poly(carbonate) analogues of poly(methyl acrylate), poly(ethyl acrylate), and poly(butyl acrylate) is described. The polymers are prepared via the salen cobalt(III) complex catalyzed copolymerization of CO_2 and a derivatized oxirane. All the carbonate analogues possess higher glass transition temperatures (T_g = 32 to -5 ^{O}C) than alkyl acrylates (T_g = 10 to -50 ^{O}C), however, the carbonate analogues (T_d=~230 ^{O}C) undergo thermal decomposition at lower temperatures than their acrylate counterparts (T_d=~380 ^{O}C). Additionally, we synthesized constitutionally isomeric poly(alkyl carbonates) in which the pendant ester group is in the reverse orientation to the backbone. Compared to the acrylate derivative, the reverse analogues possess lower glass transition temperatures (T_g = 24 to 0 ^{O}C). However, the polymerization reactions are 10X more efficient and with more polymer produced than the cyclic carbonate byproduct. The poly(alkyl carbonates) exhibit compositional dependent adhesivity, and two of the analogues possess comparative peel strength to Duct Tape® and Scotch Tape®. Finally, the poly(carbonate) analogues degrade into glycerol, alcohol, and CO_2 in a time and pH dependent manner with the rate of degradation accelerated at higher pH conditions, in contrast to the poly(acrylate)s.

Poly(alkyl acrylate)s are commodity polymers used in the pharmaceutical, cosmetic, automotive, adhesive, electronics, textiles, plastics, and paint industries.[1–5] For example, formulations of these poly(acrylate)s are used as pressure-sensitive adhesives (PSAs) in consumer-grade tapes, baby diapers, medical bandages, etc.[6,7] The PSA sector is among the fastest growing in the adhesive market, and new formulations with increased adhesivity, degradability, or stimuli-responsive characteristics are of interest.[8] However, their wide-spread industrial use on the multi-ton scale affords a significant non-degradable waste stream in society due to their all aliphatic carbon backbone.[9] As mounting plastic waste affects all aspects of life on earth, it is important to take into consideration a polymer's complete lifecycle from synthesis, to use, to degradation.[10,11] We hypothesize that introducing a cleavable carbonate linkage within the poly(acrylate) backbone will give a degradable polymer while maintaining key properties, such as adhesivity (Figure 1).

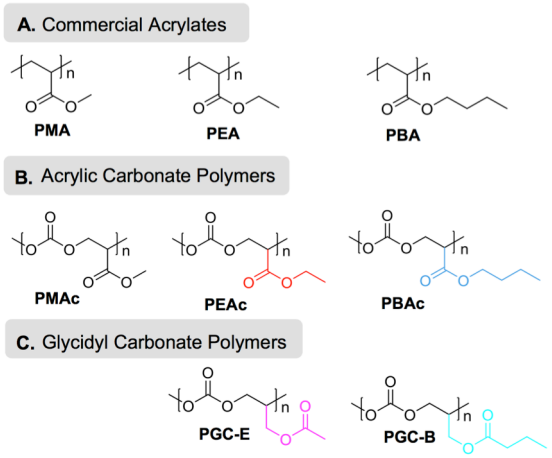

Figure 1. Commercially available poly(acrylate)s (A) poly(methyl acrylate) (PMA), poly(ethyl acrylate) (**PEA**), and poly(butyl acrylate) (**PBA**) their corresponding glycidate carbonates (B) poly(methyl acrylate carbonate) **PMAc**, poly(ethyl acrylate carbonate) **PEAc**, poly(butyl acrylate carbonate) **PBAc**, and glycidyl isomers (C) poly(glycidyl ethyl ester carbonate) **PGC-E** poly(glycidyl butyl ester carbonate) **PGC-B**.

The insertion of a carbonate moiety into the backbone of these acrylate polymers introduces an inherent glycidate or glycerol substructure allowing the carbonate analogue polymers to degrade into safe natural metabolites.(e.g., carbon dioxide, glycerol, glycidates, alcohols, and benign acids). Furthermore, given the polymer structure, we propose that these polymers can be synthesized via a green renewable process using CO_2 compared to a free radical polymerization reaction.[12,13] Herein we report the synthesis and characterization of poly(carbonate) analogues of poly(methyl acrylate) (**PMA**), poly(ethyl acrylate) (**PEA**), and poly(butyl acrylate) (**PBA**) by the copolymerization of CO_2 and the corresponding alkyl glycidate. Additionally, we describe the role pendant chain steric interactions and electronics play in monomer reactivity as well as the properties of the resultant polymers via the study of two constitutionally isomeric polymers where the pendant group esters are in opposite orientation (Figure 1).

Polymers incorporating a glycerol backbone are of significant interest due to their degradability, biocompatibility, and chemical tunability.[14–23] Glycerol is listed as Generally Recognized As Safe (GRAS) by the Food and Drug Administration, and as such, linear, branched, hyperbranched, and dendritic polyglycerols are being investigated for a wide-variety of medical and non-medical use.[24–33]

To install the carbonate moiety within the polymer back-bone, we selected a polymerization methodology pioneered and brought to fruition by Coates,[34] Darensbourg,[35] Frey,[36] Inoue,[37,38] Lu,[39,40,] and Nozaki.[41,42] Specifically, the poly(carbonate)s were synthesized via the copolymerization of an oxiranyl monomer and CO_2 using a metal salen catalyst with a quaternary ammonium salt, *rac*-[SalcyCo^{III}DNP]DNP, as shown in scheme 1 (SI page 5). Polymer selectivity was determined by ^{1}H NMR spectroscopy as the ratio of the polymeric methine hydrogen to the cyclic carbonate methine hydrogen. Turn over frequency (TOF) was calculated as

[*] A. Beharaj, I. Ekladious, Prof. M.W. Grinstaff
Departments of Chemistry, Biomedical Engineering, and Medicine
Boston University
Boston, MA 02215 (USA)
E-mail: mgrin@bu.edu
Homepage: http://people.bu.edu/mgrin

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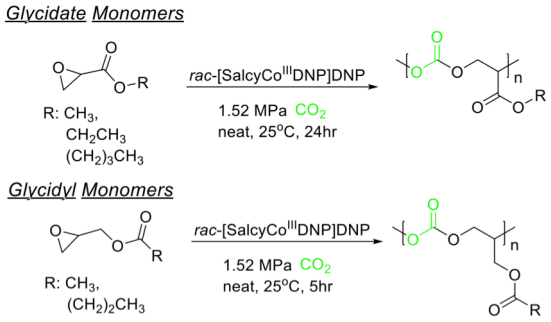
([product]/[product + monomer])·catalyst loading·h^{-1} as determined by ^{1}H NMR (SI figure 1). Finally, number average molecular weight and dispersity were determined via GPC analysis in THF with polystyrene standards.



Scheme 1. CO_2 catalysed via a cobalt salen complex (*rac*-[SalcyCo^{III}DNP]DNP) to yield polycarbonates. Please note that the polymerization conditions in scheme 1 enable comparisons between the various monomers. Optimization tables for all of the monomers can be found in SI tables 1-5.

The carbonate acrylate mimetics polymerize with low TOF values in the presence of the cobalt salen catalyst (1000:1 monomer: catalyst loading) at 25 °C and 1.54 MPa of CO_2 to give **PMAc**, **PEAc**, and **PBAc** (M_n=7.3 to 10.6 kg/mol with narrow dispersities <1.2) and significant formation of the cyclic carbonate (Figure 2 and Table 1). Of the three monomers, the methyl ester glycidate displays the highest polymer selectivity of 72%, compared to 54% for the ethyl ester and 48% for the butyl ester monomers. The catalytic TOF of the glycidate epoxides decreases with increasing carbon number of the pendant ester (24, 15 and 5.6 h^{-1} for methyl, ethyl, and butyl respectively). These low TOF values are similar to the value reported for the polymerization of poly(benzyl glycidate carbonate) (TOF = 11 h^{-1}) under the same temperature and catalyst loading.[20] Upon screening the polymerization conditions, similar trends are observed for all monomers. Raising the reaction temperature increases turnover rates but diminishes polymer selectivity, preferring the formation of cyclic carbonate. Increasing catalyst loading affords a bell curve with an optimal polymer selectivity centered at 500:1 mono-mer:catalyst loading (SI Tables 1-3).

Next, we investigated the copolymerization of CO_2 and the corresponding oxiranyl glycidyl monomers where the pendant

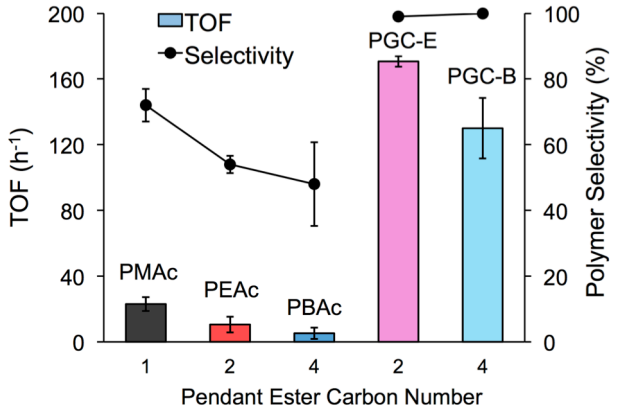


Figure 2. Polymerization efficiency of epoxide monomers with CO_2 and rac-[salcyCoIIIDNP]DNP. Reactions were performed in neat monomer (10 mmol) in an 8 mL autoclave under 1.52 MPa of CO_2 with catalyst loading of 1000:1 at 25 °C. N=3, Avg ± STD.

group esters are in the opposite orientation to the epoxide used above. These epoxide monomers are less sterically crowded and the electron withdrawing effect of the carbonyl is removed, while still preserving the ester functionality in the resulting polymer (Figure 1). The ethyl glycidyl ester and butyl glycidyl ester monomers efficiently polymerize in the presence of the cobalt salen catalyst (1000:1 monomer: catalyst loading) at 25 °C under 1.54 MPa of CO_2 with significantly greater TOF values (up to 10 fold) to give the corresponding polymeric constitutional isomers with moderate molar mass (M_n = 5.9 kg/mol to 9.9 kg/mol) and low dispersities of <1.2 (Figure 2 and Table 1). A similar trend in TOF and selectivity, to that of the glycidate polymerization, is observed with the values decreasing with increasing carbon number of the pendant ester (ethyl and butyl: TOF=171 h^{-1} and 129 h^{-1} and selectivity 99% and >99%, respectively). Decreasing the monomer:catalyst loading gives higher TOF values (with the optimal ratio being 2000:1) while increasing the temperature affords more cyclic carbonate (SI tables 4-5).

The low TOF values and polymer molar mass observed

Table 1. Thermal Properties of Acrylates and Carbonates.

Polymer	M_n(Kg/mol) [a]	Đ(M_w/M_n)	T_g(°C) [b]	T_d(°C)[c]
PMA	26	1.9	10	389
PEA	99	1.8	-27	384
PBA	95	1.7	-50	376
PMAc	7.3	1.2	17	236
PEAc	10.6	1.2	32	244
PBAc	9.8	1.3	-5	237
PGC-E	9.9	1.2	24	214
PGC-B	5.9	1.2	0	228

[a] Molar mass and dispersity are determined by GPC analysis with polysty-rene standards. [b] The glass transition is measured via DSC. [c] Thermal decomposition is determined from the TGA curve at 50% weight loss.

with the ester glycidate polymerizations are likely a consequence of the carbonyl group alpha to the methine carbon of the epoxide affording increased: 1) steric hindrance during the polymerization reaction; and 2) reactivity of the more substituted methine carbon of the epoxide via the electron withdrawing effects from the adjacent carbonyl. In support of this interpretation, Darensbourg *et al.* reported a low TOF of 9.3 h^{-1} for the synthesis of poly(tert-butyl 3,4-dihydroxybutanoate carbonate) which is an oxirane containing a bulky side chain.[43] Additionally, gaussian model (B3LYP, NBO) of the epoxide LUMO of the methine carbon-oxygen sigma* is lower than the methylene carbon-oxygen sigma* (SI figure 21). This effect is also experimentally observed, as ^{13}C NMR of glycidyl polymers exhibit 100% head-to-tail polymer backbone formation, indicating nucleophilic attack only on the least substituted side of the epoxide. However, ^{13}C NMR of the glycidate polymers display head-to-tail, tail-to-tail, and head-to-head regiosequences as well, indicating nucleophilic attack on the more substituted carbon is also occurring. (SI figures 12-16).

All the polymers exhibit bimodal distributions (SI figure 19A) due to residual water molecules (e.g., in the reactor chamber) starting new polymer chains through nucleophilic

attack of the epoxide. This is a known phenomenon in these reactions as previously discussed by Darensbourg.[44] Additionally, Maldi-ToF chain-end analysis indicates the main distribution corresponds to a hydroxyl initiator and hydroxyl terminal group, while the minor distribution is initiated with dinitrophenolate (from the catalyst) and a hydroxyl terminal group. (SI 19B). Although bimodal, these polymers exhibit narrow dispersities (<1.2) when integrating over both peaks. The polymers, like the poly(alkyl acrylate)s, are soluble in polar aprotic solvents such as dimethylformamide, tetrahydrofuran, dichloromethane, dimethylsulfoxide and acetonitrile, while not soluble in relatively polar protic solvents such as water and methanol.

We hypothesize that the proximity of the carbonyl functionality to the polymer backbone in **PMAc**, **PEAc**, and **PBAc** will restrict polymer motion leading to enhanced crystallinity, greater decomposition temperatures (T_d), and higher glass transition temperatures (T_g) compared to **PGC-E**, and **PGC-B**, as well as **PMA**, **PEA** and **PBA**. At room temperature, **PMA** is a pliable solid with a T_g of 10 °C, while **PEA** and **PBA** are viscous liquids and possess lower T_g values of -27 °C and -50 °C respectively. No melting and/or crystallization temperatures are observed for **PMA**, **PEA** and **PBA**. In contrast, **PMAc**, **PGC-E**, and **PEAc** are brittle solids at room temperature with T_g = 17, 24, and 32 °C, respectively. All of the carbonate analogues possess higher T_g than their corresponding poly(acrylate) derivatives (Table 1). This finding is attributed to the sp2 hybridization of the carbonate in the backbone limiting bond rotation, and, thus, leading to greater polymer rigidity.

Additionally, **PGC-E** possesses a lower T_g (24 °C) compared to **PEAc** (32 °C). The higher T_g value for **PEAc** is likely attributed to the side-chain carbonyl group, which imparts backbone rigidity and facilitates interchain packing through dipole interactions to form a more thermally stable bulk material. Unexpectedly, **PGC-B** exhibits a higher T_g (0 °C) than **PBAc** (-5 °C), suggesting that the pendant chain carbon length dominates

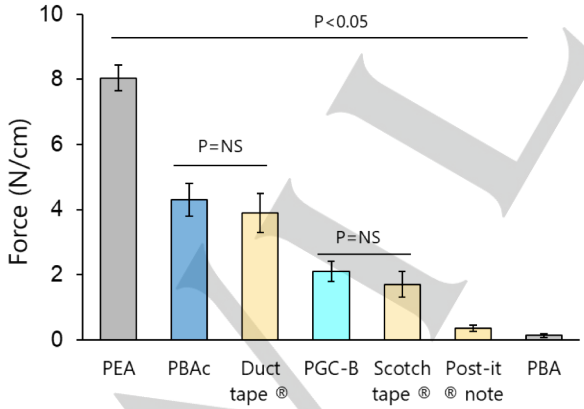


Figure 3. Peel strength of poly(acrylate)s, poly(carbonate) analogues, and commercial adhesives at 22 °C. (180° on glass following ASTM D903; N=3, Avg ± STD)

polymer packing when longer than two units. Furthermore, as mentioned above, **PBAc** contains varied regiosequences in its backbone chain, while **PGC-B** is perfectly alternating. This irregularity in **PBAc** likely leads to a larger packing volume. The polyacrylate materials exhibit higher thermal decomposition (T_d) at 50% weight loss (~380 °C) compared to all of the carbonate analogues (~225 °C).

The cytotoxicity of all the acrylate and carbonate polymers was evaluated against NIH 3T3 fibroblast cells at a high concentration of 2.5 mg/mL for 24 hours in transwell plates (SI figure 22). One-way ANOVA testing ($p > 0.05$) revealed no statistical significance between the control and polymer groups, indicating that the polymers do not leech cytotoxic compounds.

To determine the effect of introducing a carbonate linkage into the poly(alkyl acrylate) structure on the adhesive properties, peel tests were conducted at 180° between glass (SiO_2) and A4 paper (Figure 3). Only room temperature viscous polymers were examined. **PBA** exhibits the weakest peel strength (0.13 N/cm) while **PEA** possess the highest (8.04 N/cm). The poly butyl carbonate analogues, **PBAc** and **PGC-B**, are stronger adhesives than **PBA**, but weaker than **PEA**. The relative enhancement in adhesivity with the carbonate polymers likely reflects increased polymer-polymer van der walls forces and dipole interactions compared to the aliphatic poly(acrylate)s. **PBAc** (4.3 N/cm) and **PGC-B** (2.1 N/cm) exhibit comparable adhesive strength to commercial Duct Tape, (3.9 N/cm, 3M 2929) and scotch tape (1.7 N/cm, 3M 810), respectively. All of the carbonate and acrylate polymers display cohesive failure in testing, consistent with failure in the bulk layer of the material.

Aliphatic polymers are immune to most degradation methods and are only degraded by specific microbes. The process itself is long and, thus, polyacrylates exhibit main chain degradation in soil at a rate of 0.12% per 6 month, if at all.[45] In contrast, polycarbonates are known to degrade via UV radiation, oxidative cleavage, water erosion, as well as microbial, thus, polycarbonate life expectancy peaks at 3 years.[46] To evaluate the effect of introducing a carbonate linkage into the polymer backbone on degradation, studies with **PEAc**, **PGC-E**, and **PEA** were conducted over a 35 day period (Figure 4). The polymers were dissolved in a THF/water solution of 3:1 v/v %, and the number average molecular weight (M_n) was monitored via GPC analysis as a function of time. The pH of the buffer solution was varied from 5 to 9 so as to cover a range of environmental and biomedical relevance.

The molar mass of **PEA** remained relatively constant over the one month period at all three pH ranges (although some pendant ester hydrolysis is occurring) as the initial and final M_n were not statistically different from each other (One way ANOVA, $p > 0.05$). Indeed, there was significant error in the acrylate data due to high dispersity of the commercial acrylate polymer. Both **PEAc** and **PGC-E** showed appreciable degradation in all three conditions. Degradation occurred fastest at pH 9 and slowest at pH 5 for both polymers. **PGC-E** exhibited the fastest degradation rates with $t_{1/2}$= 2, 18, and >35 days for pH 9, 7, and 5, respectively. **PEAc** exhibited degradation with $t_{1/2}$= 33, >35, >35 days for pH 9, 7, and 5, respectively. **PGC-E** degraded faster than **PEAc** in all three buffers. Additionally, none of the polymers degraded in neat organic solvent (THF) for a span of 30 days (data not shown). As the degradation products are CO_2 and benign alcohols and acids, these ecologically friendly products are part of a renewable cycle (Figure 4.). As more than 260 million metric tons of plastic products are made per annum[47], tailoring polymers for faster or controlled degradation is critical to meet the ever-increasing demand for plastic goods in a growing world economy.

In conclusion, five novel carbonate polymers that structurally mimic widely utilized commercial poly(acrylate)s are described. The alkyl glycidate and glycidyl ester poly(carbonate)s are synthesized via copolymerization of the corresponding epoxide and CO_2 using a cobalt(III) salen catalyst. The polymerization efficiency is greater for the glycidyl monomers with TOF values ten times larger, along with less cyclic carbonate formation. The reported methodology is amenable to preparing polymers possessing varied alkyl ester chain lengths with narrow dispersities. The thermal and degradation properties of these two constitutional isomer polymers are significantly different. The **PMAc**, **PEAc**, and **PBAc** polymers possess higher T_gs than their **PGC-E/B** counterparts as well as higher T_gs than the commercial poly(acrylate)s. Additionally, the carbonates retain the adhesive properties of their acrylate analogues. Introduction of the carbonate linkage within the polymer backbone provides a means for polymer degradation of both polymers unlike the poly(acrylate)s. Due to the degradable nature and the relatively benign degradation products, these polymers add to the repertoire of known biodegradable and biocompatible carbonates, and will be of interest for applications in the biomedical/pharmaceutical and consumer product space.

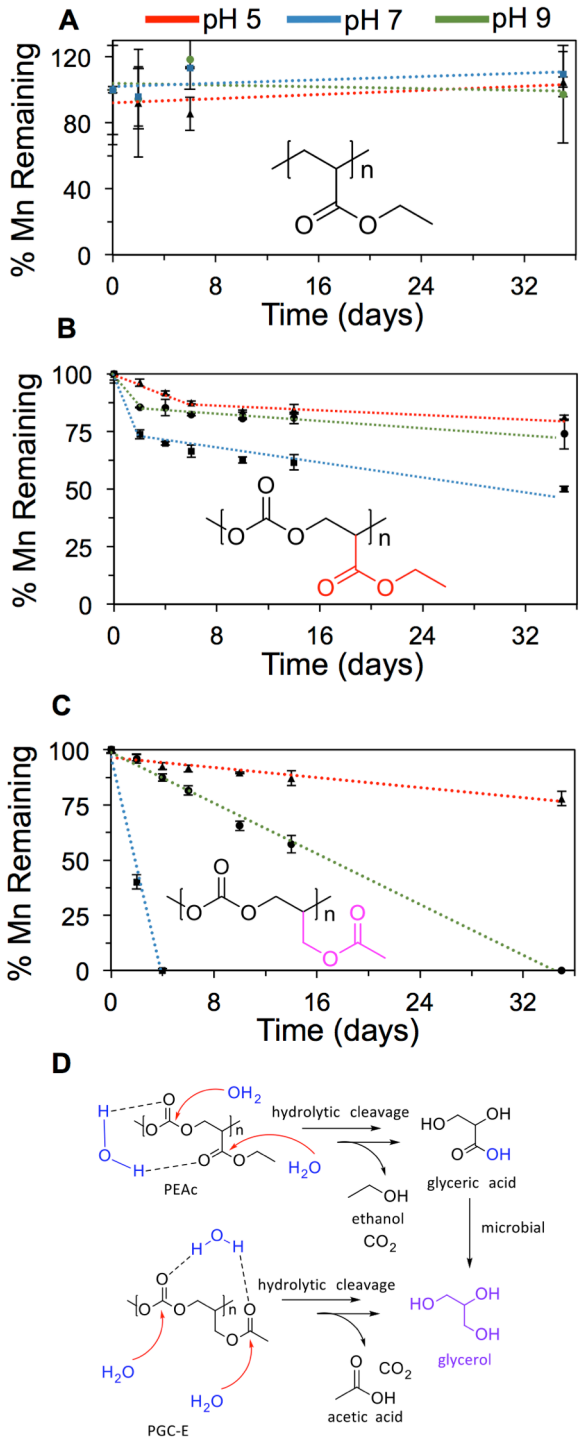


Figure 4. Degradation curves of **PEA** (A), **PEAc** (B), and **PGC-E** (C) at pH 5, 7, and 9 in 1:3 water/THF mixture. Proposed degradation routes of polycarbonates into glycerol (D).

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Keywords: polycarbonates • pressure sensitive adhesive • carbon dioxide • polyacrylates • degradable • glycerol

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ORCID
Anjeza Beharaj 0000-0003-4686-8123
Iriny Ekladious 0000-0003-1192-1414
Mark W. Grinstaff 0000-0002-5453-3668

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COMMUNICATION

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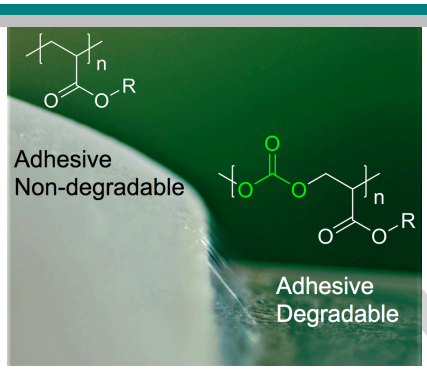

*Author(s), Corresponding Author(s)**

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Title

Degradable poly(alkyl glycidate carbonate)s, synthesized via the salen cobalt(III) complex catalyzed co-polymerization of CO_2 and glycidate, are novel pressure sensitive adhesives.