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Communication

Degradation of Polyacrylates by One-Pot Sequential Dehydrodecarboxylation and Ozonolysis

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Cite This: *J. Am. Chem. Soc.* 2023, 145, 10480−10485

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ABSTRACT: We establish a synthetically convenient method to degrade polyacrylate homopolymers. Carboxylic acids are installed along the polymer backbone by partial hydrolysis of the ester side chains, and then, in a one-pot sequential procedure, the carboxylic acids are converted into alkenes and oxidatively cleaved. This process enables the robustness and properties of polyacrylates to be maintained during their usable lifetime. The ability to tune the degree of degradation was demonstrated by varying the carboxylic acid content of the polymers. This method is compatible with a wide range of polymers prepared from vinyl monomers through copolymerization of acrylic acid with different monomers including acrylates, acrylamides, and styrenics.

Polyacrylates are regularly used in a number of applications including packaging, paints, coatings, adhesives, and sealants.[1−10] One of the most attractive features of polyacrylates is their durability, which arises from their chemical stability. However, the robust nature of polymers with all-carbon backbones often leads to the accumulation and persistence of post-consumer polyacrylate waste in landfills or oceans.[11−14] Accordingly, it is projected that 11 billion metric tons of plastic waste will amass in the environment by 2025.[15] Although there are economic and environmental incentives for recycling, there are limited options for treating discarded plastics.[16] Considerable efforts have focused on developing methods to recycle polymethacrylate materials through depolymerization back to monomers or triggering midchain cleavage via the formation of backbone radicals.[17−29] In contrast, significantly less progress has been made toward deconstructing polyacrylates.[30]

Presently, the primary strategy for synthesizing degradable polyacrylates entails copolymerization of the acrylate with a specialized cyclic comonomer through radical ring-opening polymerization (RROP).[31] For example, cyclic ketene acetal (CKA) monomers allow installation of hydrolyzable ester groups along the backbone.[32−35] However, CKAs are less reactive than acrylates, which often leads to compositional drift during the copolymerization.[32,35] Thus, scission of the labile esters of the resultant polymers produces oligomeric or even polymeric fragments with high dispersity. Thioesters or esters can be installed along the backbone in a more statistical manner through copolymerization with the macrocyclic thionolactone dibenzo[*c*,*e*]oxepane-5-thione (DOT) or a macrocyclic monomer that contains an allyl alkylsulfone motif (Figure 1).[36−40] Additionally, it recently was shown that photolabile coumarin dimers can be installed in the main chain to enable cleavage with UVB light.[41]

Although copolymerization with a cleavable monomer effectively imparts degradability to polyacrylate backbones, this approach is often synthetically challenging and may have detrimental effects on the properties of the polymers prior to deconstruction. For instance, preparation of degradable acrylate copolymers by RROP generally requires synthesis of a complex cyclic monomer and specific polymerization conditions to ensure the comonomers have a similar propensity to propagate by radical polymerization. An additional drawback is that incorporation of hydrolyzable or photolabile groups in the main chain inevitably impacts the

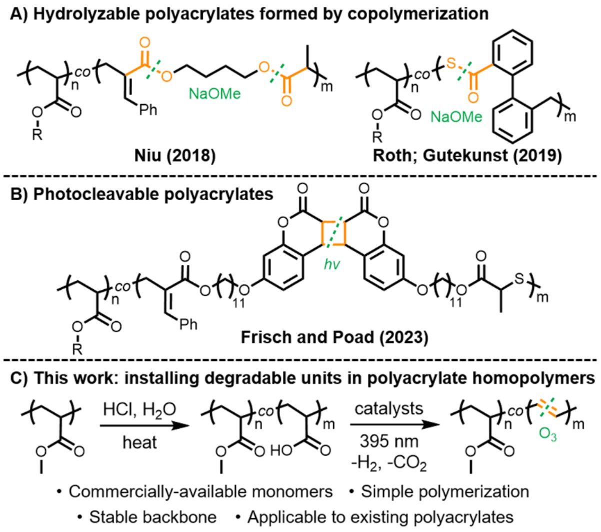
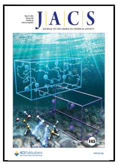


Figure 1. Methods to degrade polyacrylate backbones.

Received: March 8, 2023
Published: May 8, 2023



https://doi.org/10.1021/jacs.3c02497

thermomechanical properties of polyacrylate materials and decreases their stability and longevity.[37,39] Therefore, it would be beneficial to have a technique to efficiently degrade polyacrylates without relying on nonacrylate comonomers. Here, we present a strategy that involves hydrolysis, followed by dehydrodecarboxylation of polyacrylate homopolymers, to install cleavable alkene moieties in the backbone. In this way, the structure and properties of polyacrylates will be preserved during use, degradability can be introduced when the materials are ready to be discarded, and the approach is directly applicable to existing polyacrylates.

It has been reported that iridium, acridinium, or acridine photocatalysts can be paired with cobaloxime, a cooperative transition metal catalyst, to transform carboxylic acids into olefins, in the absence of stoichiometric oxidants.[42−48] When decarboxylation is catalyzed by acridine, the acridine forms a hydrogen-bond complex with the carboxylic acid and catalyzes O−H-hydrogen atom transfer (HAT), removing the need for the formation of carboxylates.[48] The alkyl radicals generated by decarboxylation then experience C−H-HAT with the cobaloxime to furnish alkenes. We previously implemented dual catalysis by acridine and cobaloxime to afford external alkenes in copolymers through decarboxylative elimination of methacrylic acid (MAA) units.[27] In the current work, we show that acrylic acid (AA) copolymers provide direct access to acetylene (A) copolymers, which are degradable.

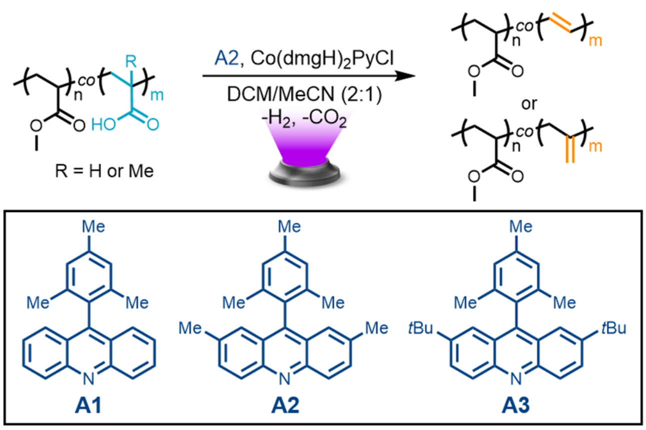
Ozonolysis is the standard method for cleaving alkenes and is extensively applied at many scales due to its operational simplicity and broad substrate scope.[49−52] Additionally, ozonolysis is less expensive than protocols that involve osmium tetroxide, ruthenium, or manganese catalysts and avoids the generation of toxic transition metal waste.[53−56]

Besides serving as degradable macromolecular structures, A copolymers with acrylate units also provide access to other functional acrylate copolymers. We envision that the backbone alkenes will be amenable to hydroesterification, hydroamination, hydration, hydrohalogenation, and other reactions.[57−60] Moreover, acrylate-A copolymers have better solubility, processability, and stability than polyacetylene (PA) homopolymers, indicating that, without any further modification, they may function as valuable PA precursors and derivatives.[61,62]

To evaluate the decarboxylative elimination of carboxylic acid side chains to form internal alkenes in polymer backbones, several copolymers containing approximately 20 mol % AA were synthesized by reversible addition−fragmentation chain transfer (RAFT) polymerization. We synthesized copolymers of AA with methyl acrylate (MA),[27] *tert*-butyl acrylate (*t*BA), *N,N*-dimethylacrylamide (DMA), and styrene (S). In general, in each of these copolymerizations, the comonomers were consumed at similar rates, confirming that the AA units were consistently incorporated throughout the polymer formation (Figures S1−S3). The pseudo-first-order kinetic plots were roughly linear, indicating that the copolymerizations had constant radical concentrations. In addition, the proportional relationships between the molecular weights and conversions of the growing polymers, monomodal gel permeation chromatography (GPC) traces, and low dispersities (1.12 to 1.29) illustrated that the polymerizations were controlled (Table S1, Figures S1−S10). Although a controlled radical polymerization is not necessary to synthesize copolymers with AA units, narrow molecular weight distributions facilitate assessment of chain scission.

With several AA copolymers in hand, we next examined dehydrodecarboxylation of the copolymer of MA and AA ($P(MA\text{-}co\text{-}AA)_{19\%}$). We found that the optimal reaction conditions included 9-mesityl-2,7-dimethylacridine (A2, 12 mol %) and $Co(dmgH)_2PyCl$ (12 mol %) cocatalysts, a solvent mixture of dichloromethane (DCM) and acetonitrile (MeCN), and irradiation by a purple LED (395 nm) at room temperature (fan cooling) (Table 1 and Figures S14−S15).

Table 1. Optimization of the Dehydrodecarboxylation Reaction



Polymer	Deviation from Conditions[c]	$M_{n,f}$ (g/mol)[d]	$Đ_f$	Alkene Yield (%)[e]
1[a]	None	21,200	1.32	74
1	No light	[f]	[f]	0
1	No A2	[f]	[f]	0
1	A1 instead of A2	21,300	1.63	48
1	A3 instead of A2	20,400	1.33	60
2[b]	8 mol % catalysts	21,100	1.25	Quant.

[a] 1 is $P(MA\text{-}co\text{-}AA)_{19\%}$. [b] 2 is $P(MA\text{-}co\text{-}MAA)_{22\%}$. [c] The reaction was conducted with A2 (12 mol %) and $Co(dmgH)_2ClPy$ (12 mol %) in a mixture of DCM and MeCN (2 mL, 2:1 v/v%) under irradiation by 395 nm light for 15 h. [d] $M_{n,f}$ was the molecular weight of the polymers after dehydrodecarboxylation. [e] The degree of alkene formation was estimated by ^1H NMR spectroscopy. [f] No reaction occurred.

Analysis of the ^1H NMR spectrum of the newly formed $P(MA\text{-}co\text{-}A)_{19\%}$ indicated that 74% of the carboxylic acids in the precursor polymer were converted into alkenes (Table S2 and Figure S16). It should be noted that, although only one isomer of the alkenes formed is depicted in Figure 1 for simplicity, another regioisomer is possible, as shown in Figure S13. Further characterization of the dehydrodecarboxylation by GPC demonstrated that the release of CO_2 and H_2 during the reaction resulted in a decrease in the molecular weight of the copolymer (Figure S31).

Various conditions for decarboxylative elimination were evaluated to determine the optimized conditions described above. First, no reaction occurred without light irradiation or addition of a photocatalyst. Several different acridine derivatives were assessed for their efficacy as photocatalysts. Replacement of A2 with 9-mesitylacridine (A1) or 2,7-di-*tert*-butyl-9-mesitylacridine (A3) resulted in lower degrees of alkene formation in the copolymer. Gratifyingly, use of A2 instead of unsubstituted acridine led to disappearance of the small high molecular weight shoulder, likely due to coupling, that was present in the GPC trace of the decarboxylated MAA copolymer ($P(MA\text{-}co\text{-}MAA)_{22\%}$) that was previously reported

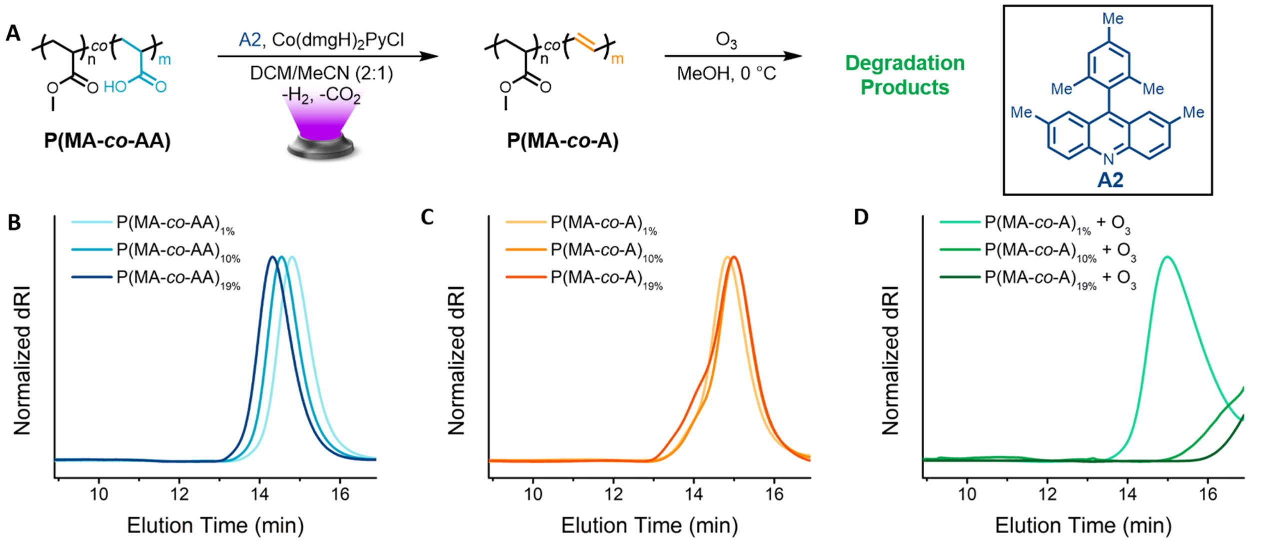


Figure 2. Degree of degradation was tuned by varying the percentage of AA units in the precursor polymer. (A) Scheme illustrating sequential dehydrodecarboxylation and ozonolysis of copolymers bearing carboxylic acids. (B) GPC traces of MA-AA copolymers with 1, 10, and 19 mol % AA. (C) GPC traces of copolymers after dehydrodecarboxylation. (D) GPC plots of degradation products resulting from ozonolysis.

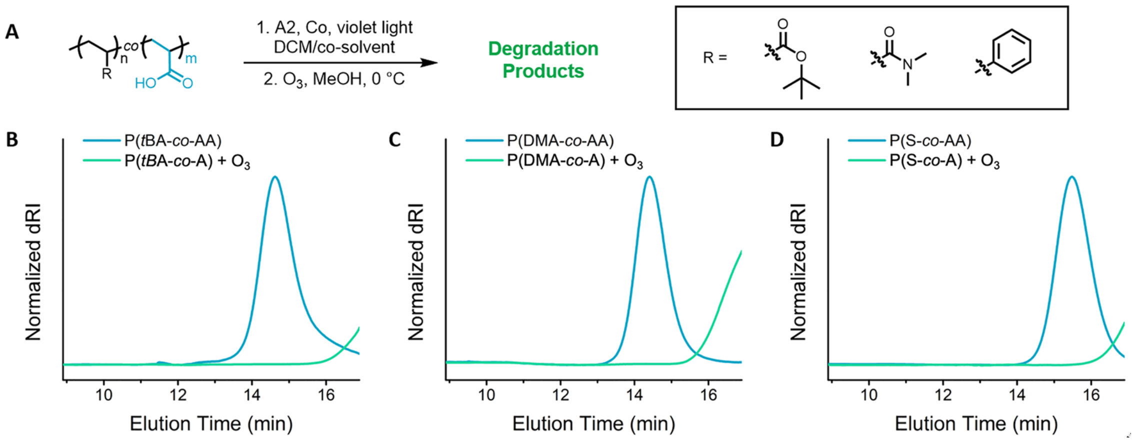


Figure 3. Degradation of copolymers of AA and several different vinyl monomers. (A) Scheme showing general conditions for degradation. GPC traces of P(*t*BA-*co*-AA) (B), P(DMA-*co*-AA) (C), and P(S-*co*-AA) (D) before and after dehydrodecarboxylation and degradation.

(Figures S17 and S34).[27] This was likely due to the higher turnover efficiency of A2.[63] During dehydrodecarboxylation, the carboxylic acid of the chain transfer agent was converted into an alkene, while the trithiocarbonate was unchanged (Figures S18 and S19).

After formation of P(MA-*co*-A)$_{19\%}$, which had cleavable alkenes along the backbone, degradation of this copolymer by ozonolysis was investigated (Figure 2). To cleave the backbone, methanol was added to the reaction mixture at 0 °C, followed by ozone. Chain scission was complete in less than 1 h, indicating that the oxidative cleavage was rapid. P(MA-*co*-A)$_{19\%}$ degraded into low molecular weight oligomers (Figures S20 and S39). Notably, the dehydrodecarboxylated polymer did not need to be purified prior to ozonolysis, greatly simplifying the degradative protocol.

Once we effectively degraded the copolymer of MA and AA containing 19 mol % AA, we went on to dehydrodecarboxylate and degrade MA-AA copolymers with 1 and 10 mol % AA for comparison (Figures 2 and S32−S33). Not surprisingly, we found that the AA content in the precursor polymers impacted the molecular weight of the degradation products. The GPC trace of degraded P(MA-*co*-A)$_{1\%}$ broadened, but did not fully shift to a higher elution time, indicating that not all of the chains were cleaved (Figure S40). While each of the chains of the starting copolymer, on average, had 2 AA units, the number of AA units per chain can vary. Thus, some chains did not have any AA units, leading to an absence of labile alkenes in those chains after dehydrodecarboxylation. In contrast, degradation of P(MA-*co*-A)$_{10\%}$ led to a much greater and complete shift of the GPC trace, and P(MA-*co*-A)$_{19\%}$ shifted even further (Figure S41). These results indicate that the size of the degradation products can be tuned by changing the AA content of the precursor polymer.

We next applied our degradation approach to several other vinyl copolymers containing AA units to demonstrate its versatility. Dehydrodecarboxylation of P(*t*BA-*co*-AA)$_{19\%}$ (M_n = 18.6 kg/mol) transformed 39% of the carboxylic acid side chains into internal alkenes (Figure 3, S21−S22, and S35). Although this polymer had a lower yield than P(MA-*co*-AA)$_{19\%}$, the alkene content was sufficient to enable cleavage of this copolymer into low molecular weight species (Figure S42). P(DMA-*co*-AA)$_{20\%}$ (M_n = 27.3 kg/mol) and P(S-*co*-AA)$_{20\%}$

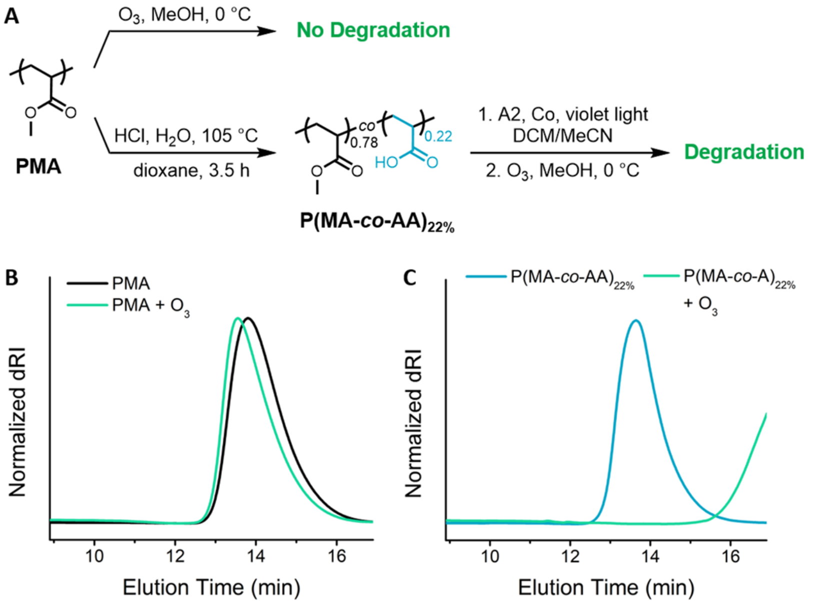


Figure 4. PMA only degraded after alkenes were installed in the backbone. (A) Scheme displaying absence of PMA degradation when exposed to ozone and formation of a degradable polymer through partial hydrolysis, followed by dehydrodecarboxylation. (B) GPC traces of PMA before and after ozone treatment. (C) GPC plots P(MA-*co*-AA)$_{22\%}$ before and after dehydrodecarboxylation and ozonolysis.

(M_n = 11.3 kg/mol) exhibited conversions of AA units to A units of 66% and 71%, respectively, indicating that amide and phenyl groups were tolerated by the reactions (Figures S23−S26, and S36−S37). Accordingly, the dehydrodecarboxylated structures of these precursors were successfully degraded by ozonolysis (Figures S43−S44). The efficient degradation was consistent with the uniform distribution of AA units throughout the backbones of the initial copolymers synthesized by RAFT. Characterization of the degradation product of P(S-*co*-A)$_{20\%}$ after workup indicated the presence of carboxylic acid end groups (Figures S27 and S28). We envision that these oligomers may be repolymerized to form biodegradable polyesters, leading to upcycling. Likely, the A copolymers may also be deconstructed through metathesis to furnish other interesting repolymerizable macromonomers.[64−66]

Finally, we demonstrated that PMA homopolymers could be degraded by introducing carboxylic acids along the backbone by hydrolyzing esters of the MA units. Partial hydrolysis of PMA was accomplished by heating with HCl and water and produced a copolymer with 22 mol % AA (P(MA-*co*-AA)$_{22\%}$, M_n = 44.4 kg/mol, M_p = 59.4 kg/mol) (Figures 4 and S11−S12 and S29).[67] We targeted a relatively low conversion of esters into carboxylic acids since 19 mol % of AA permitted degradation into small fragments. Still, the AA content can be tuned by the hydrolysis time. As expected, the robust PMA homopolymer, which lacked alkenes, did not exhibit any reduction in molecular weight during ozone treatment, confirming that chain scission did not occur. In contrast, installation of alkene groups in the backbone of the hydrolyzed copolymer enabled a decrease in molecular weight to an M_p of around 1.3 kg/mol due to oxidative cleavage of the backbone (Figures S30, S38, and S45−S46). Taken together, these data suggest that our method may be applied to commercial polyacrylates.

In summary, this work introduced a method to install degradable units in highly stable polyacrylate homopolymers. When applied to copolymers bearing AA units, dehydrodecarboxylation yielded acrylate, acrylamide, and styrene copolymers with internal alkenes under mild conditions. Ozonolysis of the A copolymers effected chain scission, giving rise to low-molecular-weight oligomers. The approach described may degrade polyacrylates present in packaging, adhesive, or coating materials. This work brings us one step closer to combating the ever-increasing amount of vinyl plastic waste polluting the environment.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c02497.

Materials, instrumentation, synthetic procedures, and additional characterization including polymerization kinetics, GPC data, and NMR spectra. (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation (DMR-1904631 and EEC-1941529). Additional support from the University of Florida is gratefully acknowledged. We thank Megan Lott for assistance with GPC analysis.

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