

Incorporation of CO₂-derived Bicyclic Lactone into Conventional Vinyl Polymers

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Abstract: The ability to copolymerize monomers vastly increases the range of accessible material properties for a specific monomer. We investigate the radical copolymerization of lactone monomer (3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one) (EVP), made from butadiene and carbon dioxide. The unique bicyclic structure provided by the EVP unit resulted in an elevation of the glass transition temperature across a range of commodity polymers and enabled the incorporation of functionality into EVP-based copolymers.

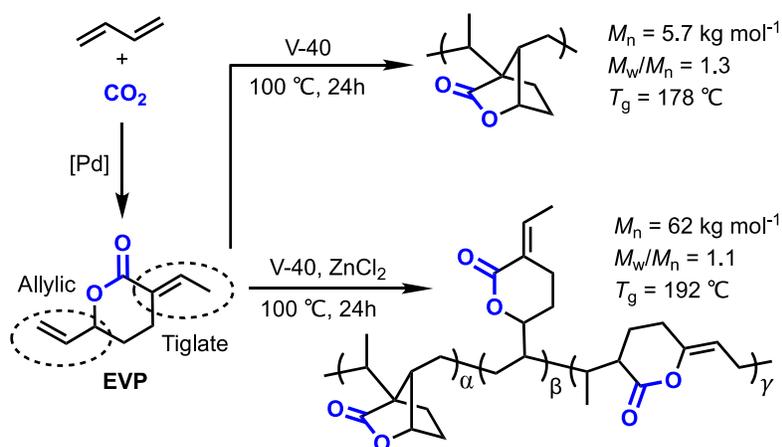


Figure 1. Synthesis and radical polymerization of EVP.

The utilization of carbon dioxide in chemical transformations has received significant attention due to the low cost, economic efficiency, abundance, and low toxicity of carbon dioxide.¹⁻² In particular, the incorporation of carbon dioxide into polymers has become an appealing route to synthesize sustainable and renewable materials.² However, the thermodynamic stability and poor reactivity of carbon dioxide has rendered most

copolymerizations kinetically unattainable. The use of epoxides as high-energy comonomers has emerged as a successful route to carbon dioxide-derived copolymers, however, the resulting polycarbonates and polyethercarbonates offer limited flexibility in polymer properties.³⁻⁵ In spite of the significant kinetic barriers associated with carbon dioxide and olefin copolymerization,⁶⁻⁷ in 2014, our group demonstrated a thermodynamic bypass to overcome the endergonic penalty of carbon-dioxide incorporation through a metastable diolefin lactone intermediate, 3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one (EVP, figure 1).⁸ While EVP had previously been synthesized,⁹⁻¹² it was believed to be inert to anionic, cationic, and radical polymerization due to the tiglate- and allylic-like olefins, which are known to be difficult to homopolymerize. Fortunately, we found that, in the presence of a radical initiator, EVP underwent cyclopolymerization via alternating incorporation of the tiglate unit and the allyl unit to produce a bicyclic repeating unit. The butadiene-CO₂ copolymer contained 33 mol% carbon dioxide (29 wt%) and a high glass transition temperature (T_g) of 178 °C (Figure 1). In 2017, the use of molecular oxygen as an initiator was reported to be effective by Lin *et al.*¹³ Additionally, the lactone has been demonstrated to undergo ring-opening (co)polymerization, copolymerization with ethylene, and thiol-ene cross linking to form polymer networks providing several novel routes to develop CO₂ based materials.¹⁴⁻²⁰

Considering the versatility of radical polymerization and the number of commodity polymers derived from it, we aimed to explore the radical copolymerization of EVP with the most common monomers used today. Given that the rigid bicyclic structure polyEVP is likely to be the origin for its high T_g ,²¹⁻²² we reasoned that copolymerization of EVP could increase the T_g s of relevant commodity polymers and produce a novel class of more sustainable polyolefins (Figure 2). Furthermore, copolymerization with commercially-available functional monomers could enable facile post-polymerization modification, greatly expanding the scope of olefin-carbon dioxide copolymers.

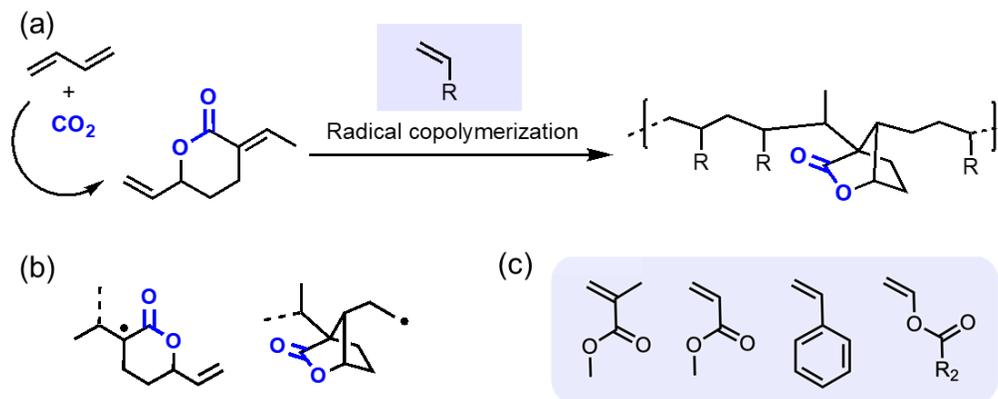


Figure 2. (a) Radical copolymerization of EVP with various commodity monomers. (b) Radical intermediates for incorporation of EVP. (c) Polar monomers employed in this study: methyl methacrylate (MMA), methyl acrylate (MA), styrene (Sty), vinyl chloroacetate (VAcCl) and vinyl acetate (VAc).

One of our interests was the copolymerization of EVP with methyl methacrylate (MMA), aiming at enhancement of the glass transition temperature of poly(methyl methacrylate) (PMMA). Since its discovery in the early 1930s, PMMA has been one of the major transparent thermoplastics, used in applications as a light-weight alternative for silica-based glass. In some specific applications, especially in the fields of optics or electronics, the relatively low T_g of PMMA is considered problematic since it causes undesirable distortion that can inhibit the desired functions.²³ One commonly employed strategy to enhance the T_g of PMMA is the incorporation of bulky and rigid monomers, such as maleimides,²⁴⁻²⁸ adamantly methacrylate,²⁹ and isobornyl methacrylate.³⁰⁻³¹ Based on the rigid nature of the unique bicyclic structure formed by the polymerization of EVP, we assumed that the introduction of this moiety inside the PMMA chains would reduce the free movement of the polymer chains, eventually leading to higher T_g .

With this hypothesis, we investigated the copolymerization of MMA and confirmed its effect on the thermal properties of PMMA. Copolymerization was first explored with equimolar MMA/EVP ($f_{\text{MMA}} = 0.5$) and 1 mol% 1,1'-azobis(cyclohexane-1-carbonitrile) (V-40) under emulsion polymerization at 100 °C, conditions we previously found optimal for achieving the highest yield and molecular weight of the bicyclic lactone homopolymer. After 24 h, polymeric materials were isolated by precipitation into methanol. The existence of both bicyclic lactone and MMA units was confirmed by ¹H NMR spectroscopy which indicated ~20% incorporation of the bicyclic lactone (Table 1, entry 1& Figure 3A). Size exclusion chromatography (SEC) analysis revealed a bimodal distribution (Figure 3B), and differential scanning calorimetry (DSC) exhibited the presence of two T_g values of

132 °C and 188 °C (Figure S1). Notably, the lower temperature of 132 °C is higher than the standard value for atactic PMMA, ~105 °C.²⁷ Separation of the polymer mixture by preparative SEC afforded two eluents; one was a homopolymer of MMA (M_n 110,000, M_w/M_n 1.5) and the other was a material containing both MMA and ~28% EVP units (M_n 23,000, M_w/M_n 1.2) (Figure S2 (A, B)). The latter exhibited two T_g values 130 °C and 181 °C, implying the existence of a copolymer with blocky structure (Figure S2 (C, D)). Similar results were obtained using bulk conditions at the same temperature and polymerization time (Table 1, entry 2 & Fig. S3).

Table 1. Copolymerization of EVP with MMA^a

Entry	f_{MMA}	MMA conversion (%) ^c	Temp. (°C)	Time (h)	M_n (kg mol ⁻¹) ^d	M_w/M_n	Lactone incorp. (%) ^e	T_g (°C) ^f
0	0	-	100	24	5.7	1.3	100	178
1 ^b	0.5	>95	100	24	20.0	1.6	28	132 & 188
2	0.5	>95	100	24	32.2	1.5	19	131 & 186
3	0.5	90	100	1	49.0	1.3	3.9	118
4	0.2	50	90	1	29.3	1.3	13	116
5	0.1	45	90	1	20.1	1.4	22	111
6 ^e	0.5	-	90	6	26.3	1.4	18	126

^aTypical reaction conditions: A mixture of EVP (1.0 mmol), MMA, and V-40 (0.1 mmol) were stirred under nitrogen and the polymeric materials were collected by reprecipitation from methanol. ^bEmulsion conditions used: A mixture of EVP (2.5 mmol), MMA (2.5 mmol), potassium persulfate (KPS, 0.250 mmol) in 15 mM sodium dodecylsulfate (SDS) solution (12.5 mL) was stirred and then the polymeric materials were reprecipitated from methanol. ^cConversion monitored by ¹H NMR. ^dMolecular weights determined using SEC in DMF with LiBr. ^eDetermined by ¹H NMR analysis of the polymers obtained by reprecipitation. ^fDetermined by DSC. ^eSlow addition of MMA over 6 hours to keep f_{MMA} low throughout copolymerization.

By monitoring monomer conversion during the copolymerization, we found that MMA was nearly entirely consumed at ~90% conversion within one hour of copolymerization, whereas little to no conversion of the lactone was observed. We therefore speculated that during copolymerization, rapid homopolymerization of MMA first occurred, followed by copolymerization of MMA and EVP once MMA concentration became low. This is likely due to the combined steric hindrance of the tiglate-like olefin and the poor reactivity of the allyl acetate olefins with MMA ($r_{\text{allyl acetate}} = 0$, $r_{\text{MMA}} = 23$).³²⁻³³ Indeed, stopping the copolymerization after 1 hour (~95% MMA conversion), gave a copolymer with a unimodal molecular weight distribution by SEC and 3.9% EVP incorporation (Table 1 entry 3 and Figure 3 (C, D)). While the SEC charts of copolymers in entries 1 and 2 were

bimodal, the ones in the other entries were unimodal (See SI). Additionally, only one T_g was observed at 118 °C in entry 3 (Figures S4). By lowering the feed ratio of MMA (f_{MMA}) from 0.5 to 0.2 or 0.1 (Table 1, entries 4 and 5), the EVP incorporation was increased to 13% and 22%, respectively, after 1 h of copolymerization. Despite the increased incorporation of EVP, the resulting copolymer actually exhibited a *decrease* in T_g (Figure S6), likely due to the lower molecular weight of copolymers produced with high initial feeds of EVP. In order to access higher molecular weight with a high EVP incorporation, MMA was added slowly over several hours to keep the overall fraction of MMA low. This resulted in both a slight increase in molecular weight and resulted in a T_g of 126 °C (Table 1, entry 6, Figure S7).

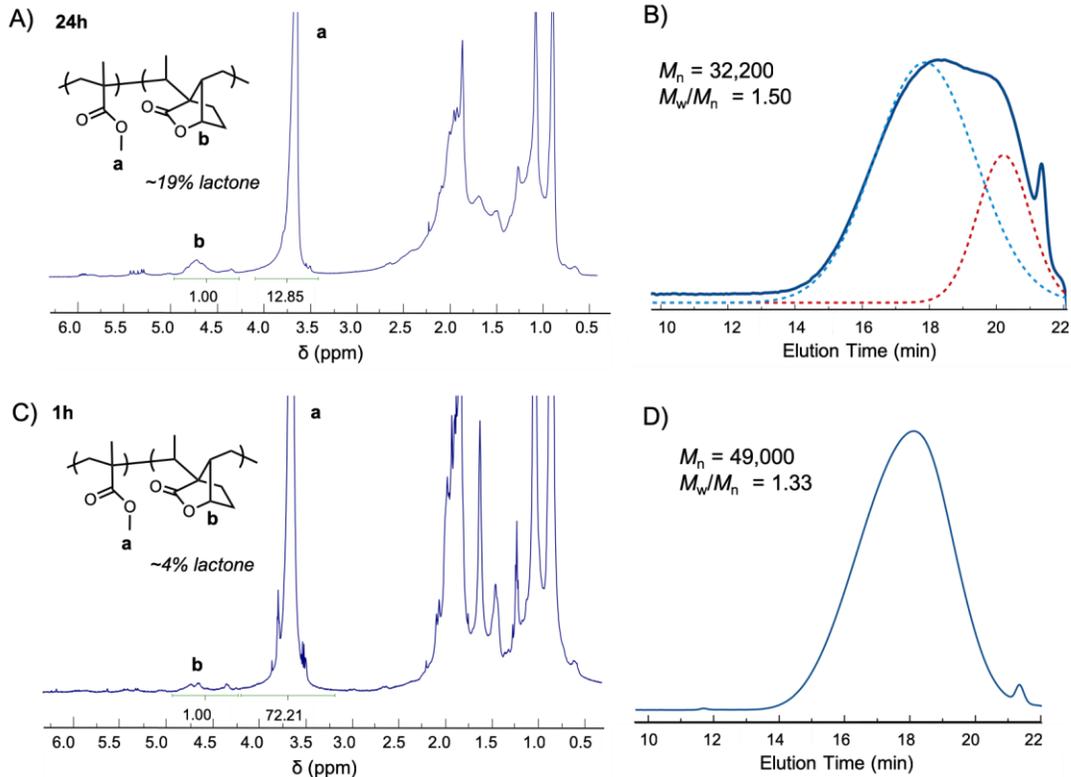


Figure 3. Copolymerization of EVP with MMA: equimolar copolymerization at 100 °C for 24 h resulting in 19% EVP incorporation by ^1H NMR (CDCl_3) (A) and a bimodal distribution by SEC (dashed lines represented deconvolution of chromatogram) (B); and copolymerization at 100 °C for 1 h resulting in 4% EVP incorporation by ^1H NMR (CDCl_3) (C) and a unimodal distribution by SEC (D).

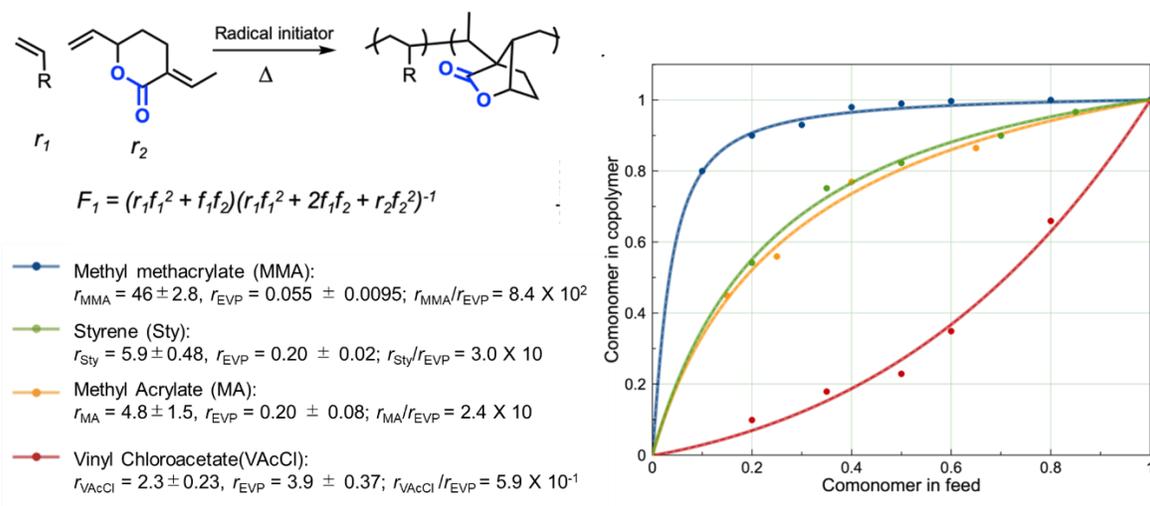


Figure 4. Copolymer composition curves for the copolymerization of EVP in bulk conditions with A) methyl methacrylate at 90 °C (blue), B) styrene at 80 °C (green), C) methyl acrylate at 70 °C (yellow), and D) vinylchloroacetate (red) at 90 °C with 1 mol% initiator. Nonlinear line fitting to the nonlinear least-squares fitting curve was used to determine reactivity ratios.

To gain further understanding of the copolymerization behavior of EVP, we investigated the free radical copolymerizations of EVP with a variety of monomer classes including: styrene (Sty), methyl acrylate (MA), and vinyl chloroacetate (VAcCl) at 90, 80, and 100 °C, respectively. Polymerization temperature was varied for each system to prevent comonomer evaporation and/or auto-initiation. VAcCl was used instead of vinyl acetate (VAc) due to the lack of distinguishable peaks in the ^1H NMR spectrum of the copolymer. The mole fraction of monomers in the feed were kept between 0.1 and 0.9 and total monomer conversions were kept <30% to prevent errors associated with compositional drift. Total monomer conversion was calculated based on ^1H NMR of the initial and final samples, and polymer composition (F_1) was determined using ^1H NMR of the isolated polymer precipitate. Reactivity ratios were calculated by comparing the copolymer composition of isolated copolymers (F_1) to the initial monomer feed and applying a nonlinear fit to the Mayo-Lewis relationship $F_1 = (r_1 f_1^2 + f_1 f_2)(r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2)^{-1}$

As expected from our previous results, MMA demonstrated a significantly higher reactivity over EVP, $r_{\text{MMA}} = 46$, $r_{\text{EVP}} = 0.05$, further clarifying the poor incorporation of EVP during copolymerization (Figure 4). Copolymerization with other more activated, but less sterically hindered monomers such as styrene (Sty) and methyl acrylate (MA), still demonstrated preferential polymerization of the comonomer to EVP ($r_{\text{sty}} = 5.0$, $r_{\text{EVP}} = 0.20$; $r_{\text{MA}} = 4.8$, $r_{\text{EVP}} = 0.20$), however with more favorable copolymerizability compared to

MMA. Different radical initiators were used to ensure efficient copolymerization. While similar reactivity is known for allyl acetate olefins and MA ($r_{\text{MA}} = 5$, $r_{\text{allyl acetate}} = 0$), copolymerization of S with EVP is enhanced compared to allyl acetate ($r_{\text{allyl acetate}} = 0$, $r_{\text{S}} = 20$). This may indicate that the presence of the tiglate-like olefin helps stabilize the EVP radical to enhance its copolymerizability with more activated monomers. EVP copolymerization with VAcCl, a less activated monomer, demonstrated good copolymerizability with slightly higher preference of EVP copolymerization, $r_{\text{VAcCl}} = 2.3$ and $r_{\text{EVP}} = 3.9$. Despite the success in EVP/VAcCl copolymerization, copolymerization between EVP and VAc required excess VAc (Table 2, entries 14 and 15) to achieve good EVP incorporation, possibly due to the lower boiling point of VAc (72 °C) and the high temperature needed to polymerize EVP.

The tunability of EVP content in copolymerizations with MA, S, VAcCl and VAc enabled us to look at the effect of EVP incorporation on resulting copolymer T_{gs} . As shown in Table 2, for each copolymerization system, increasing EVP content resulted in increased T_{g} . Figure 5 depicts the DSC traces of poly(methyl acrylate) (PMA) with increasing EVP content. These results indicate that the bicyclic structure of PEVP can indeed increase the T_{gs} of conventional copolymers. The tendency nicely matches to the predicted values by the Fox equation (See SI). It is worthy of noting that only bicyclic lactone units were detected in the main-chain of the obtained copolymers.

Table 2. Copolymerization of EVP with MA, S, VAcCl and VAc, and effect of EVP incorporation on copolymer glass transition temperatures.^a

Entry	Comonomer (mole fraction)	Initiator (mmol%)	Temp. (°C)	Time (h)	M_n (kg mol ⁻¹) _b	M_w/M_n	Lactone incorporation (%) ^c	T_g (°C) ^d
1	MA (0.65)	AIBN (1)	70	2	115.5	1.6	13.7	48
2	MA (0.40)			1.3	43.4	1.9	23	77
3	MA (0.50)			2	60.0	1.8	45	94
4	MA (0.30)			2	25.5	1.5	50	118
5	MA (0.15)			2	20.5	1.4	55	127
6	S (0.85)	AIBN (1)	80	24	19.5	1.5	3.5	94
7	S (0.70)			24	20.1	1.5	10.2	105

8	S (0.50)			24	19.8	1.4	17.9	119
9	S (0.35)			24	18.8	1.3	25	132
10	S (0.20)			24	18.9	1.2	46	162
11	VAcCl (0.80)	V-40 (10)	100	24	35.4	1.23	34	100
12	VAcCl (0.50)			24	19.8	1.18	80	140
13	VAcCl (0.20)			24	15.9	1.16	90	150
14	VAc (0.95)	V-40 (10)	70	24	71.8	1.10	13	67
15	VAc (0.91)			24	45.0	1.22	48	143

^a A mixture of EVP, comonomer, and radical initiator was heated and stirred under nitrogen. ^b Molecular weights determined using SEC in DMF with LiBr with a calibration curve based on polystyrene. ^c Determined by ¹H NMR or quantitative ¹³C NMR. ^d Determined by DSC.

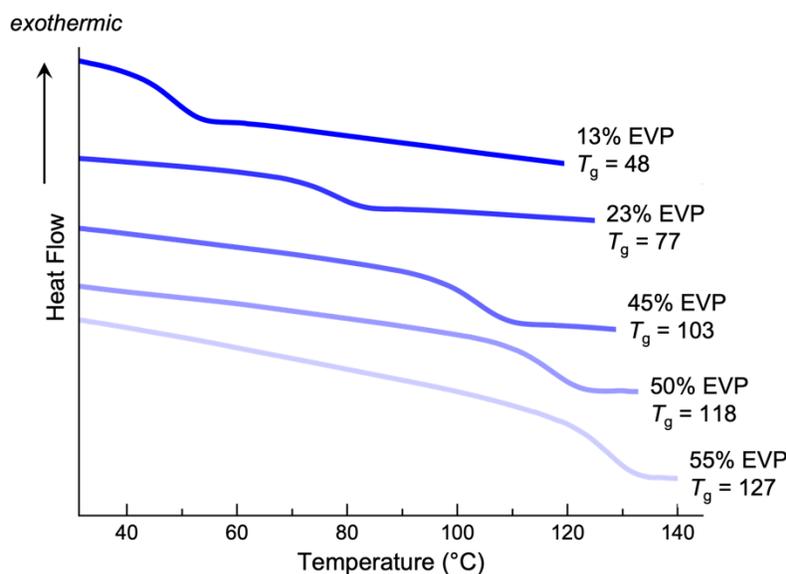


Figure 5. DSC traces of PMA with increasing EVP incorporation.

The use of VAcCl as a comonomer enabled access to a much broader range of materials through hydrolysis to synthesize poly(vinyl alcohol) (PVA) copolymers or substitution of the chloro- group with nucleophiles such as sodium azide to access “click” functional copolymers. Copolymers of p(VAcCl)-*co*-p(EVP) were demonstrated to undergo hydrolysis using potassium carbonate and substitution using sodium azide without compromising the bicyclic lactone structure in the backbone of the copolymer. Figure 6 shows the FTIR chart of p(VAcCl)-*co*-p(EVP) (top), hydrolyzed p(VA)-*co*-

p(EVP) (middle) and azide-functional p(VAcN₃)-co-p(EVP) (bottom). NMR spectra further confirm the successful hydrolysis and post-polymerization modification of the copolymers with retention of the bicyclic lactone structure (Fig. S12 and 14).

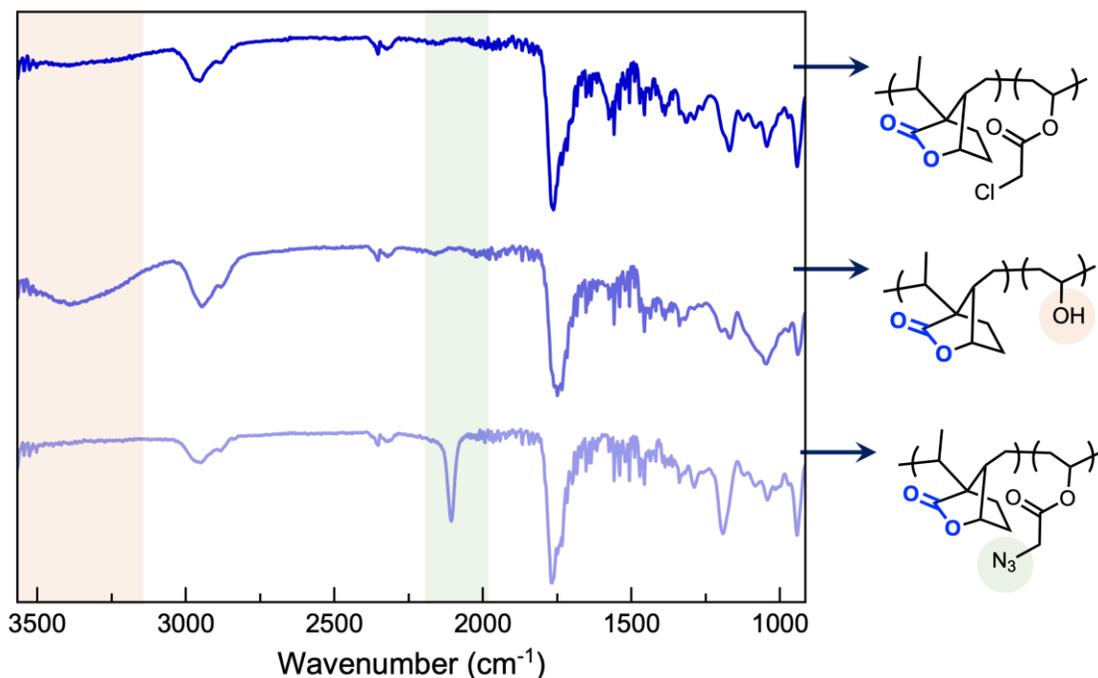


Figure 6. . FTIR spectrum of p(VAcCl)-co-p(EVP) (top) and copolymers after hydrolysis (middle) and substitution with sodium azide (bottom).

In conclusion, we demonstrated that copolymerization of EVP with conventional vinyl monomers results in copolymers with a bicyclic lactone structure in the polymer backbone. Reactivity ratios of EVP with MMA, MA, Sty, VAcCl were calculated using a nonlinear fit to the Mayo-Lewis equation ($r_{\text{MMA}} = 46$, $r_{\text{EVP}} = 0.05$; $r_{\text{MA}} = 4.8$, $r_{\text{EVP}} = 0.20$; $r_{\text{sty}} = 5.0$, $r_{\text{EVP}} = 0.20$; $r_{\text{VAcCl}} = 2.3$ and $r_{\text{EVP}} = 3.9$). Incorporation of EVP into polystyrene, polymethylacrylate, polyvinylchloroacetate and polyvinylacetate was demonstrated to increase the glass transition temperatures of traditional copolymers. Finally, hydrolysis and post-polymerization modification of p(VAcCl)-co-p(EVP) demonstrated the ability to access a larger range of EVP-based copolymers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental details, materials, methods, NMR spectra, SEC and DSC data. (PDF)

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Notes

The authors declare no competing financial interest.

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References

1. Liu, Q.; Wu, L.; Jackstell, R.; Beller, M., Using carbon dioxide as a building block in organic synthesis. *Nat. Commun.* **2015**, *6*, 5933.
2. Grignard, B.; Gennen, S.; Jérôme, C.; Kleij, A. W.; Detrembleur, C., Advances in the use of CO₂ as a renewable feedstock for the synthesis of polymers. *Chem. Soc. Rev.* **2019**, *48*, 4466-4514.
3. Kamphuis, A. J.; Picchioni, F.; Pescarmona, P. P., CO₂-fixation into cyclic and polymeric carbonates: principles and applications. *Green Chem.* **2019**, *21*, 406-448.
4. Wang, Y.; Darensbourg, D. J., Carbon dioxide-based functional polycarbonates: Metal catalyzed copolymerization of CO₂ and epoxides. *Coordin. Chem. Rev.* **2018**, *372*, 85-100.
5. Lu, X.-B.; Ren, W.-M.; Wu, G.-P., CO₂ Copolymers from Epoxides: Catalyst Activity, Product Selectivity, and Stereochemistry Control. *Acc. Chem. Res.* **2012**, *45*, 1721-1735.
6. Price, C. J.; Reich, B. J. E.; Miller, S. A., Thermodynamic and Kinetic Considerations in the Copolymerization of Ethylene and Carbon Dioxide. *Macromolecules* **2006**, *39*, 2751-2756.
7. Moha, V.; Cozzula, D.; Hölscher, M.; Leitner, W.; Müller, T. E., A DFT Study on the Copolymerization of CO₂ and Ethylene: Feasibility Analysis for the Direct Synthesis of Polyethylene Esters. *ChemSusChem* **2016**, *9*, 1614-1622.

8. Nakano, R.; Ito, S.; Nozaki, K., Copolymerization of carbon dioxide and butadiene via a lactone intermediate. *Nat. Chem.* **2014**, *6*, 325-331.
9. Sasaki, Y.; Inoue, Y.; Hashimoto, H., Reaction of carbon dioxide with butadiene catalysed by palladium complexes. Synthesis of 2-ethylidenehept-5-en-4-olide. *J. Chem. Soc., Chem. Commun.* **1976**, 605-606.
10. Musco, A.; Perego, C.; Tartari, V., Telomerization reactions of butadiene and CO₂ catalyzed by phosphine Pd(0) complexes: (E)-2-ethylidenehept-6-en-5-olide and octadienyl esters of 2-ethylidenehepta-4,6-dienoic acid. *Inorg. Chim. Acta* **1978**, *28*, L147-L148.
11. Behr, A.; Henze, G., Use of carbon dioxide in chemical syntheses via a lactone intermediate. *Green Chem.* **2011**, *13*, 25-39.
12. Sharif, M.; Jackstell, R.; Dastgir, S.; Al-Shihi, B.; Beller, M., Efficient and selective Palladium-catalyzed Telomerization of 1,3-Butadiene with Carbon Dioxide. *ChemCatChem* **2017**, *9*, 542-546.
13. Liu, M.; Sun, Y.; Liang, Y.; Lin, B.-L., Highly Efficient Synthesis of Functionalizable Polymers from a CO₂/1,3-Butadiene-Derived Lactone. *ACS Macro Lett.* **2017**, *6*, 1373-1378.
14. Ferretti, F.; Sharif, M.; Dastgir, S.; Ragaini, F.; Jackstell, R.; Beller, M., Selective palladium-catalysed synthesis of diesters: alkoxycarbonylation of a CO₂-butadiene derived δ -lactone. *Green Chem.* **2017**, *19*, 3542-3548.
15. Chen, L.; Li, Y.; Yue, S.; Ling, J.; Ni, X.; Shen, Z., Chemoselective RAFT Polymerization of a Trivinyl Monomer Derived from Carbon Dioxide and 1,3-Butadiene: From Linear to Hyperbranched. *Macromolecules* **2017**, *50*, 9598-9606.
16. Zhang, Y.; Xia, J.; Song, J.; Zhang, J.; Ni, X.; Jian, Z., Combination of Ethylene, 1,3-Butadiene, and Carbon Dioxide into Ester-Functionalized Polyethylenes via Palladium-Catalyzed Coupling and Insertion Polymerization. *Macromolecules* **2019**, *52*, 2504-2512.
17. Garcia Espinosa, L. D.; Williams-Pavlantos, K.; Turney, K. M.; Wesdemiotis, C.; Eagan, J. M., Degradable Polymer Structures from Carbon Dioxide and Butadiene. *ACS Macro Lett.* **2021**, *10*, 1254-1259.
18. Tang, S.; Zhao, Y.; Nozaki, K., Accessing Divergent Main-Chain-Functionalized Polyethylenes via Copolymerization of Ethylene with a CO₂/Butadiene-Derived Lactone. *J. Am. Chem. Soc.* **2021**, *143*, 17953-17957.
19. Chen, L.; Ling, J.; Ni, X.; Shen, Z., Synthesis and Properties of Networks Based on Thiol-ene Chemistry Using a CO₂-Based δ -Lactone. *Macromol. Rapid Commun.* **2018**, *39*.
20. Rapagnani, R.; Dunscomb, R.; Fresh, A.; Tonks, I., Tunable and Recyclable Polyesters from CO₂ and Butadiene. *ChemRxiv* **2021**, doi: 10.33774/chemrxiv-2021-4b5js.
21. Muñoz-Guerra, S.; Lavilla, C.; Japu, C.; Martínez de Ilarduya, A., Renewable terephthalate polyesters from carbohydrate-based bicyclic monomers. *Green Chem.* **2014**, *16*, 1716-1739.
22. Liu, Y. C.; Turner, S. R., Synthesis and Properties of Cyclic Diester Based Aliphatic Copolyesters. *J. Poly. Sci.: Part A: Polym. Sci.* **2010**, *48*, 2162-2169.
23. Ali, U.; Karim, K. J. B. A.; Buang, N. A., A Review of the Properties and Applications of Poly (Methyl Methacrylate) (PMMA). *Polym. Rev.* **2015**, *55*, 678-705.
24. Kita, Y.; Kishino, K.; Nakagawa, K., Synthesis of N-cyclohexylmaleimide for heat-resistant transparent methacrylic resin. *J. Appl. Polym. Sci.* **1997**, *63*, 363-368.
25. Kita, Y.; Kishino, K.; Nakagawa, K., High-quality N-substituted maleimide for heat-resistant methacrylic resin. *J. Appl. Polym. Sci.* **1997**, *63*, 1055-1062.
26. Dong, S. S.; Wei, Y. Z.; Zhang, Z. Q., Study on the synthesis of heat-resistant PMMA. *J. Appl. Polym. Sci.* **1999**, *72*, 1335-1339.

27. Jiang, X. L.; Yan, D. Y.; Zhong, Y. L.; Liu, W. L.; Chen, Q. X., Atom transfer radical copolymerization of methyl methacrylate with N-cyclohexylmaleimide. *Polym. Int.* **2000**, *49*, 893-897.
28. Mishra, A.; Sinha, T. J. M.; Choudhary, V., Methyl methacrylate-N-chlorophenyl maleimide copolymers: Effect of structure on properties. *J. Appl. Polym. Sci.* **1998**, *68*, 527-534.
29. Matsumoto, A.; Tanaka, S.; Otsu, T., Synthesis and characterization of poly(1-adamantyl methacrylate): effects of the adamantyl group on radical polymerization kinetics and thermal properties of the polymer. *Macromolecules* **1991**, *24*, 4017-4024.
30. Yeh, S. L.; Zhu, C. Y.; Kuo, S. W., Transparent Heat-Resistant PMMA Copolymers for Packing Light-Emitting Diode Materials. *Polymers* **2015**, *7*, 1379-1388.
31. Ko, K. Y.; Hwang, S. H., Monomer composition effects on thermal properties of transparent poly(methyl methacrylate-co-isobornyl methacrylate-co-cyclohexyl maleimide) terpolymers. *J. Ind. Eng. Chem.* **2018**, *59*, 50-55.
32. Young, L. J., Copolymerization parameters. *J. Polym. Sci.* **1961**, *54*, 411-55.
33. Butler, G. B., Cyclopolymerization and cyclocopolymerization. *Acc. Chem. Res.* **1982**, *15*, 370-378.

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