

Supporting Information

Dynamic Covalent Exchange Induced Cyclization in Poly(Methacrylic Anhydride)

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IR conversion calculation

The equation in Figure S1 was used to find the conversions of the PMAA where the bounds of integration was kept constant from sample to sample.

$$\% \text{ Conversion} = 1 - \frac{\frac{\text{Ene Area}_{\text{Polymer}}}{\text{Anhydride Area}_{\text{Polymer}}}}{\frac{\text{Ene Area}_{\text{Monomer}}}{\text{Anhydride Area}_{\text{Monomer}}}} * 100$$

Figure S1. Displays the percent conversion calculation. The ene was integrated from 1660 cm⁻¹ and 1564 cm⁻¹ and anhydride was integrated from 1853 cm⁻¹ and 1660 cm⁻¹ with base line correction to find the area.

Impact of elevated polymerization temperatures

To explore if an increase in polymerization temperature would be expected to increase conversion, UV polymerizations in an oil bath at 80°C and 130°C were performed. These resulted in a 59% and 73% monomer-to-polymer conversion, respectively (IR spectra from these polymerizations is shown below in Figure 1.) However, in addition to greater monomer conversion, there is also significant dynamic covalent exchange that is induced at these temperatures, which results in a mixture of cyclic and acyclic anhydride species previously avoided through the use of bulk polymerization and low temperatures. This high temperature cyclization resulted in a decrease in the plateau T_g from 155°C to ~130°C for both polymerization temperatures tested.

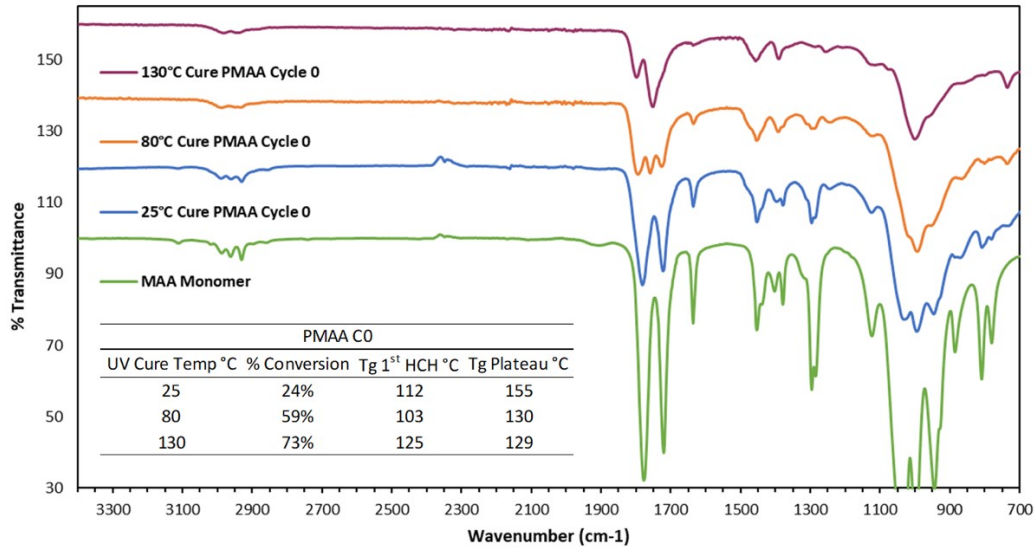


Figure S2. IR data from PMAA cycle 0 samples exposed to post-baking, along with % monomer conversion and DSC data.

Hydrolysis evaluation

Poly(methacrylic acid) is the hydrolysis product of PMAA, therefore if hydrolysis is occurring the signal in question will overlap with the carbonyl of the acid. Figure S3 shows the poly(methacrylic acid) carbonyl occurs at 1694 cm^{-1} and does not correspond to the evolved peak at 1750 cm^{-1} .

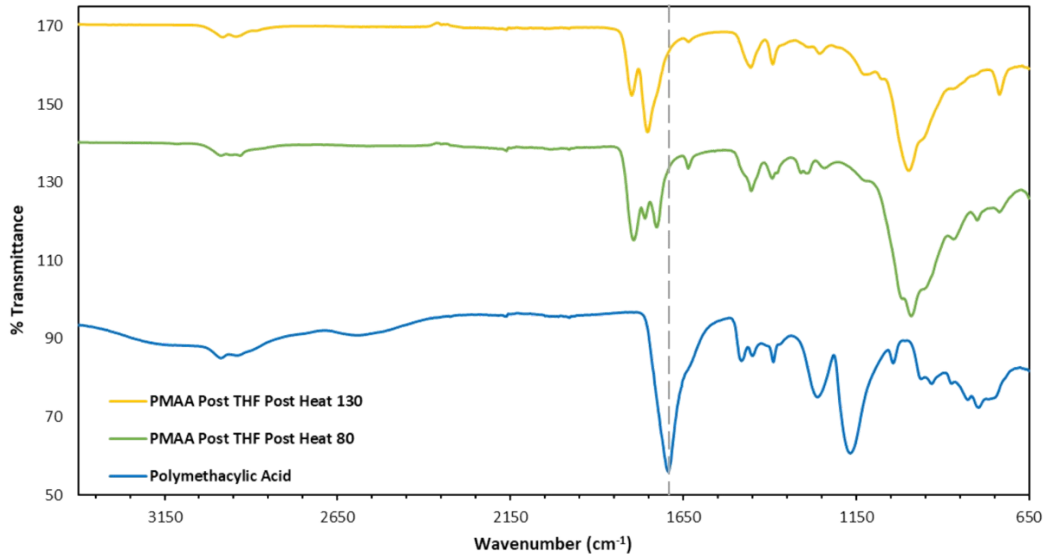


Figure S3. IR spectra illustrating the differences in carbonyl peak position for poly(methacrylic acid) and the heat treated PMAA (after THF extraction).

Small molecule computational study

Calculation type and basis set was altered to observe if the difference (Δ) between the symmetric and asymmetric stretch can be affected by calculation type and basis set. For all calculations conducted and small molecules tested (see Table S1), acyclic anhydrides result in larger differences between the symmetric and asymmetric stretch than cyclic anhydrides. Additionally, the experimental data and calculated difference correspond fairly well to each other, illustrating that the computational method can accurately and reproducibly predict the IR spectra of experimental data.

Table S1. Summary table of differences between symmetric and asymmetric anhydride stretch of cyclic and acyclic model compounds.

Type	Basis Set	Acyclic Δ (cm ⁻¹) Sym-Asym			Cyclic Δ (cm ⁻¹) Sym-Asym		
		Benzoic	Valeric	Isobutyric	3,3 Dimethyl Glutaric	Diglycolic	Glutaric
Experimental		60.0	67.7	63.8	46.9	47.2	47.1
ω B97X-D/6	6-31G'	61.0	63.7	64.0	43.8	44.3	42.0
HF	6-31G'	67.4	67.0	69.8	50.7	48.9	48.7
MP2	6-31G'	54.3	60.9	61.4	34.8	35.0	32.8
B3LYP	6-31G'	59.5	62.7	63.2	41.8	41.8	40.0
B3LYP	6-31G+	59.0	63.3	63.7	43.1	42.8	41.0
B3LYP	cc-pVDZ	65.1	68.2	67.7	37.8	39.8	36.3
B3LYP	SDD	59.6	64.4	65.0	41.8	42.3	39.5

Cyclic isomer evaluation

Calculated IR spectra were performed to determine if the 1720 cm⁻¹ and 1750 cm⁻¹ asymmetric anhydride carbonyl peak could be attributed to cyclic isomers rather than acyclic and cyclic. The isomers were modeled with bulky groups in order to further differentiate the two structures through steric hindrance (Figure S4). It was found that chirality of the cyclic isomers did not affect anhydride carbonyl stretch since the carbonyl peaks of both isomers of the achiral cyclic model compound overlap. Table S2 summarizes the difference between the symmetric and asymmetric stretches of the modeled isomers with varying calculation types and basis sets.

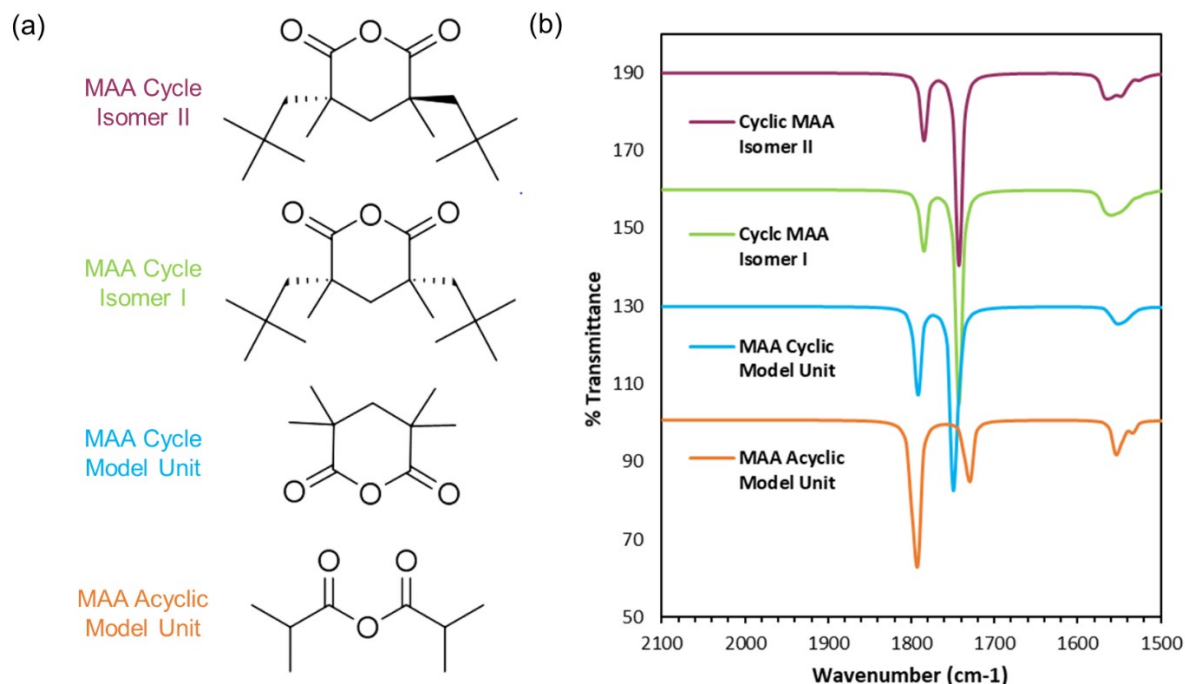


Figure S4. (a) Structures modeled to observe the effect of chirality. (b) Computational IR spectra illustrating cyclic chirality has no effect on the anhydride IR stretch.

Table S2. Summary table showing the absence of chirality effect on the anhydride IR stretch.

Type	Calculation		Acyclic Δ (cm ⁻¹)		Cyclic Δ (cm ⁻¹)		Isomer I Δ (cm ⁻¹)		Isomer II Δ (cm ⁻¹)	
	Basis Set		Sym-Asym		Sym-Asym		Sym-Asym		Sym-Asym	
ω B97X-D/6	6-31G'		64.0		47.0		42.8		42.5	
HF	6-31G'		69.8		51.2		47.0		46.7	
MP2	6-31G'		61.4		38.0		50.7		50.3	
B3LYP	6-31G'		63.2		45.0		35.1		35.0	
B3LYP	6-31G+		63.7		45.1		44.9		43.8	
B3LYP	cc-pVDZ		67.7		41.5		40.4		40.0	
B3LYP	SDD		65.0		39.3		43.6		44.8	

Exposure to ambient conditions

Anhydrides will undergo hydrolysis if exposed to water in the environment. To provide quantitative data regarding the stability of PMAA samples to ambient conditions, small pieces of polyahydride ("cycle 0" samples) were observed over 6 days either as a monolithic chunk or ground powder. In the IR spectra recorded each day (Figure S5), it can be seen that sample types showed evidence of a carboxylic acid peak (~ 1700 cm⁻¹) within 2 days. We note that the powder experienced hydrolysis at a faster rate than the chunk of polymer due to the larger surface area. In terms of how samples were handled while

collecting data for this manuscript, all samples were stored at 0°C and the exposure time to air was minimized order to avoid hydrolysis.

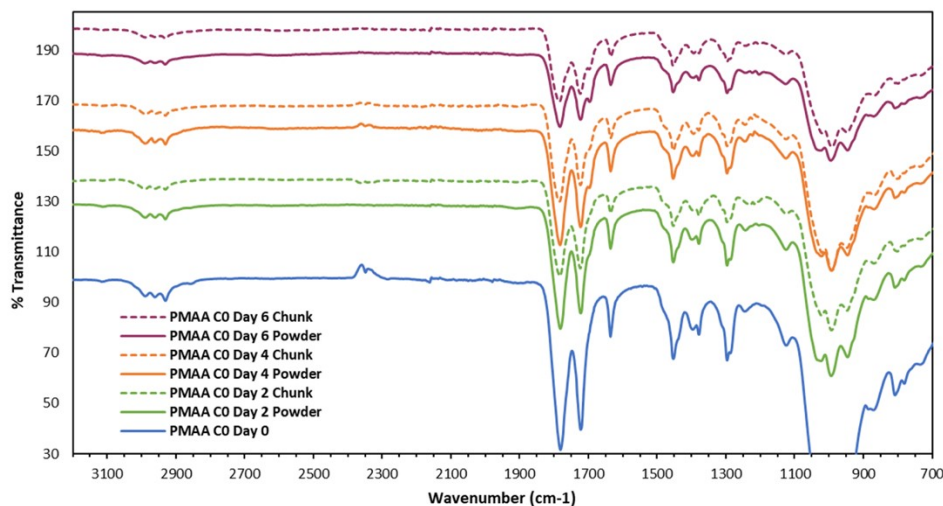


Figure S5. IR data from PMAA cycle 0 samples exposed to ambient conditions in either powder or monolithic (chunk) form. Temperatures 22-23oC, % Humidity = 46-59%.

Dynamic mechanical analysis (DMA)

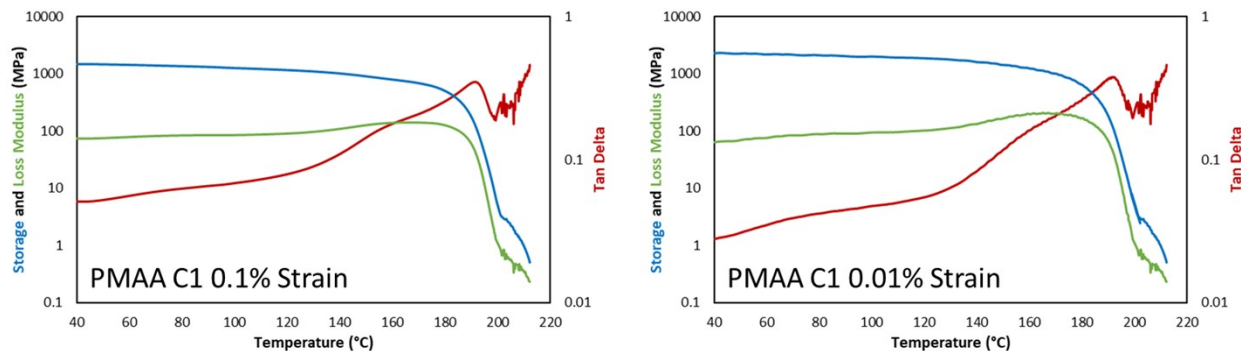


Figure S6. DMA data collected of a “cycle 1” PMAA sample using a TA Instruments Q800 DMA equipped with a dual cantilever clamp, 1N preload force, 0.1% and 0.01% strain, 1Hz frequency, 5°C/min, 5 min soak time, and 35°C to 250°C sweep.

Repeated HCH cycles in DSC analysis

The heat applied in the DSC to observe the T_g can impact the polymer through exchange and additional polymerization of unreacted C=C bonds. Figure S6 repeated HCH runs on the T_g and the “plateau” effect of PMAA C0.

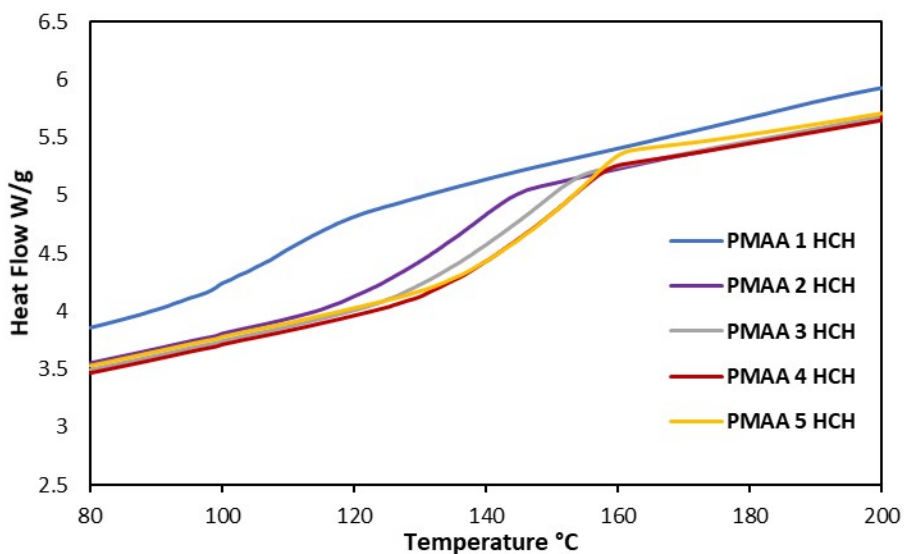


Figure S7. DSC traces illustrating the effect of repeated HCH DSC cycles on the glass transition temperature. The second heat trace of the HCH is displayed of each replicate. Exothermic is down.

Impact of high temperature recycling with lower pressure and shorter time

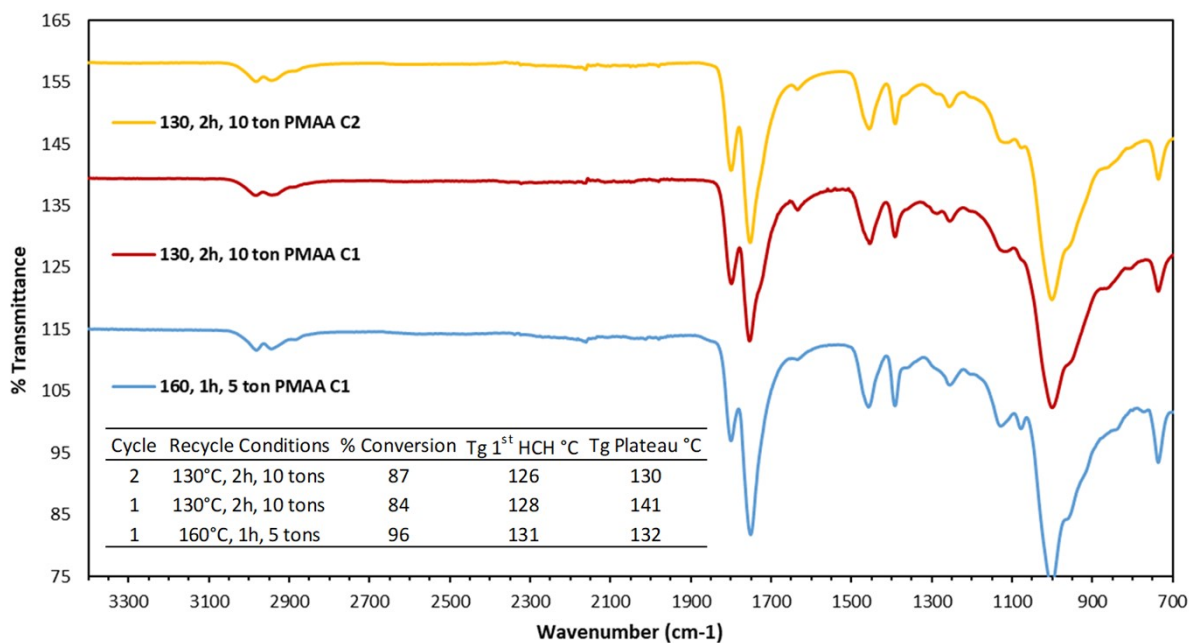


Figure S8. IR spectra and T_g data for PMAA samples exposed to different pressures and temperatures during recycling.