

At Line Analysis in the Manganese Catalysed Epoxidation of Ethylene Propylene Diene Rubber (EPDM) with H₂O₂

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Electronic Supplementary Information

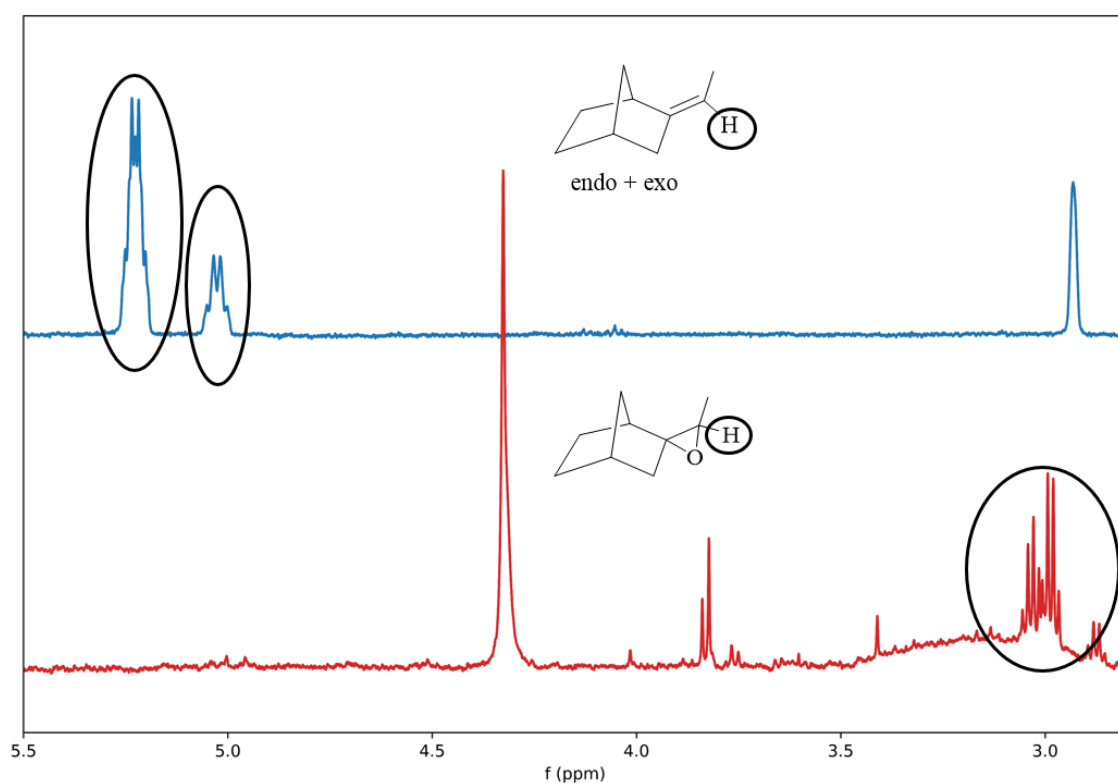


Figure S1. ¹H-NMR spectra of model compound dihydro-5-ethylidene-2-norbornene (ENBH) before and after epoxidation. Conditions: ENBH (0.125 M), 0.025 mM Mn(II)(ClO₄)₆·6H₂O, 1.25 mM picolinic acid, 2.4 mM sodium acetate, 0.125 mM 2,3-butanedione, 2.5 mM acetic acid, 3 equiv. H₂O₂ in acetone at room temperature for 1 h.

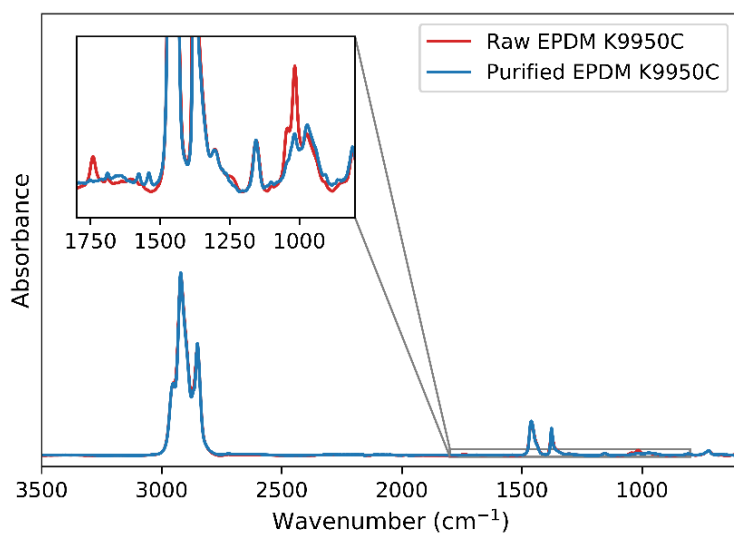


Figure S2. ATR-IR spectra show the difference in absorption of raw and purified EPDM rubber. The presence of bands at 1015 cm⁻¹, 1045 cm⁻¹ and 1250 cm⁻¹ (from C-O stretching bands) and a band at 1740 cm⁻¹ (from C=O stretching bands), indicate that an ester-containing chemical is removed upon purification.

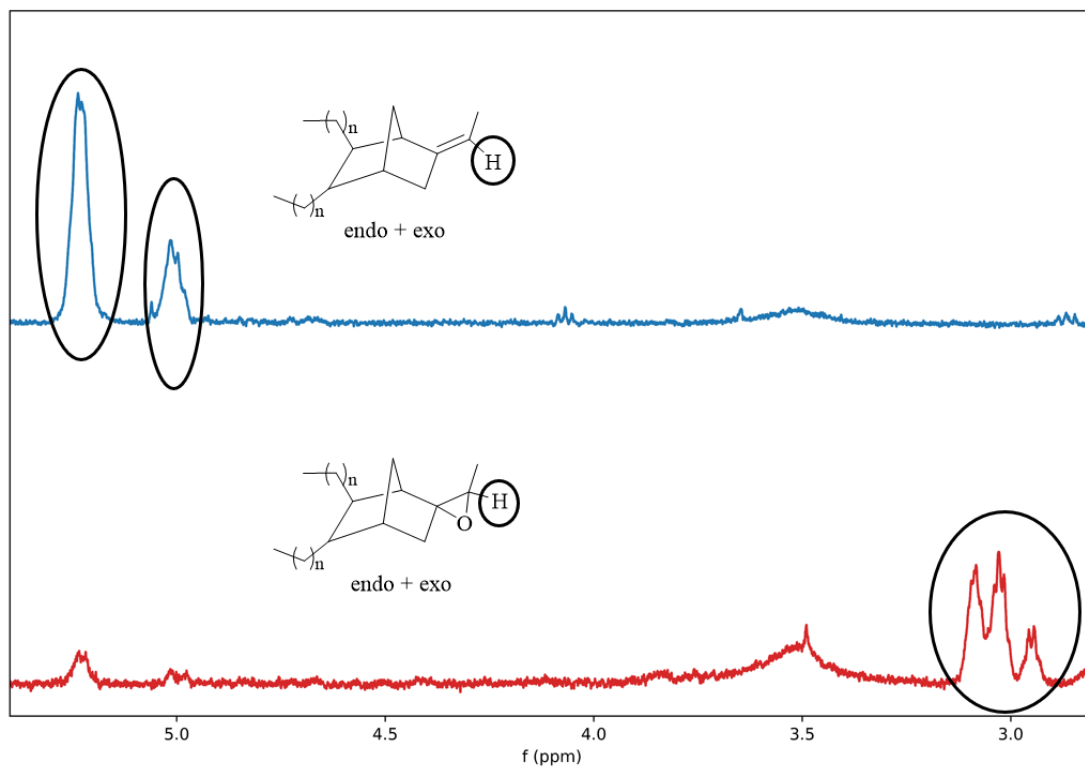


Figure S3. ¹H-NMR spectrum of the reaction mixture containing EPDM rubber before (above) and after (below) oxidation. Conditions: EPDM rubber (9 wt% **ENB**) (2.5 mM in alkene unites), 0.1 mM Mn(II)(ClO₄)₆·6H₂O, 5 mM sodium picolinate, 0.25 M 2,3-butanedione, 0.1 M acetic acid, 10 equiv. H₂O₂ in cyclohexane/cyclohexanone (50/50) at RT for 1 h.

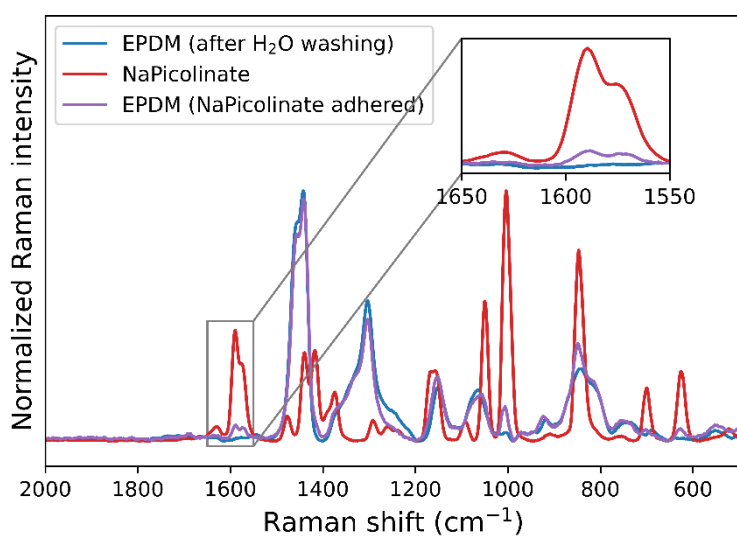
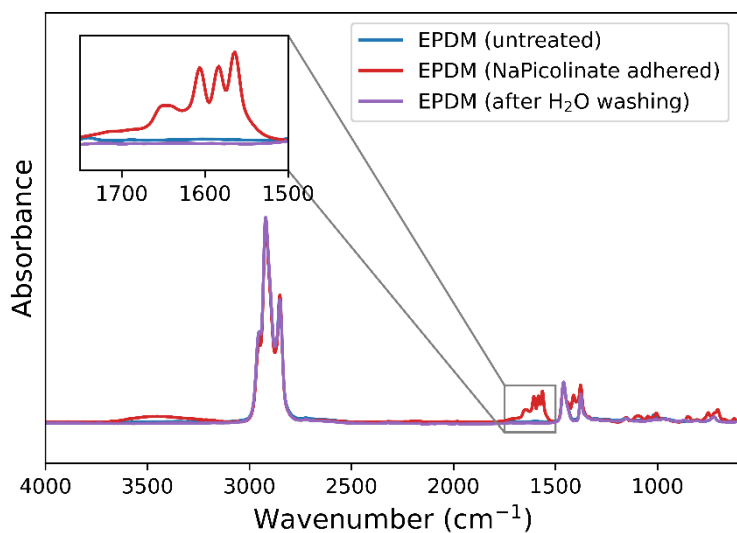
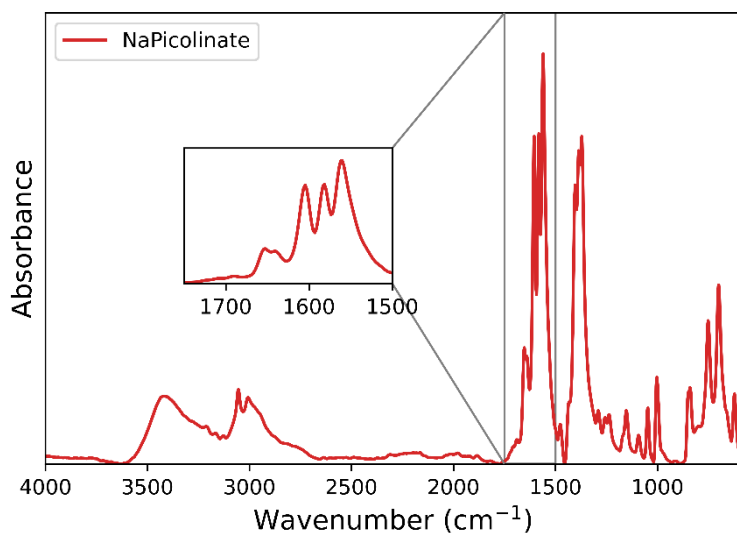


Figure S4. Top: ATR-IR spectrum of sodium picolinate; Middle: ATR-IR spectra of untreated EPDM rubber, EPDM rubber with sodium picolinate adhered and after washing the rubber with water; Bottom:

Raman spectra at 785 nm of sodium picolinate, EPDM rubber with sodium picolinate adhered and after washing the rubber with water.

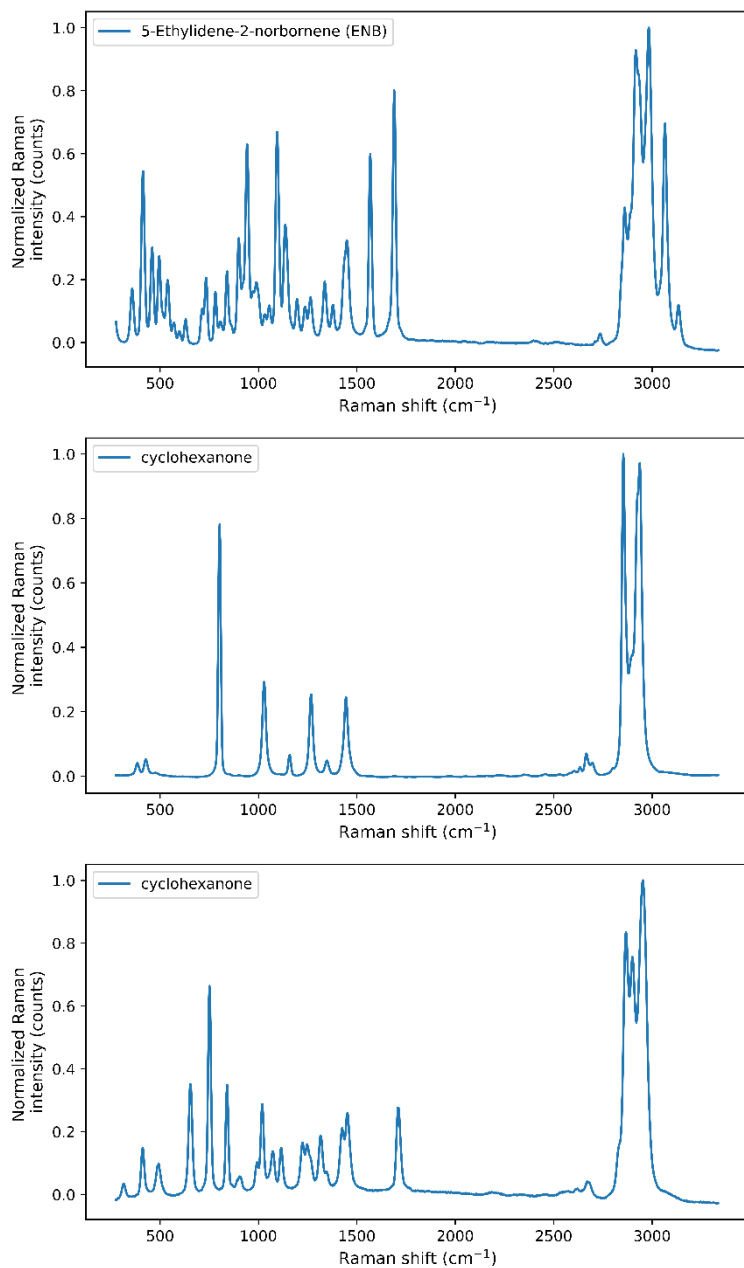


Figure S5. From top to bottom: Raman spectra at 532 nm of 5-ethylidene-2-norbornene (ENB), cyclohexane and cyclohexanone.

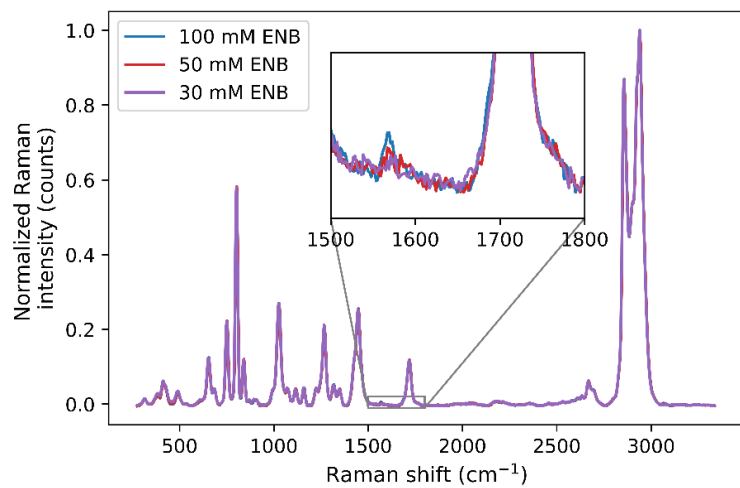


Figure S6. Raman spectra at 532 nm of 30, 50 and 100 mM 5-ethylidene-2-norbornene (ENB) in a 50/50 volume percent mixture of cyclohexane/cyclohexanone.

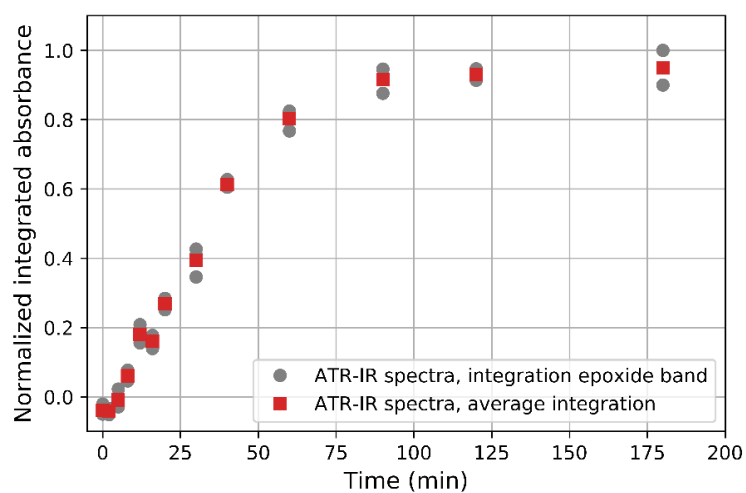
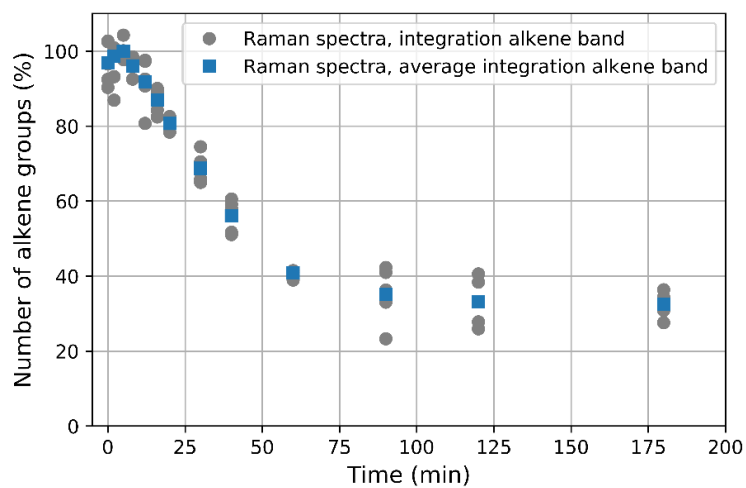


Figure S7. Accuracy of the Raman and ATR-FTIR spectroscopic measurements. Several Raman and infrared spectra were recorded of the same EPDM rubber sample, but on different points on the sample. The average of the five (for Raman spectra) or three (for ATR-FTIR spectra) integrations are presented with a blue and red dot, respectively.

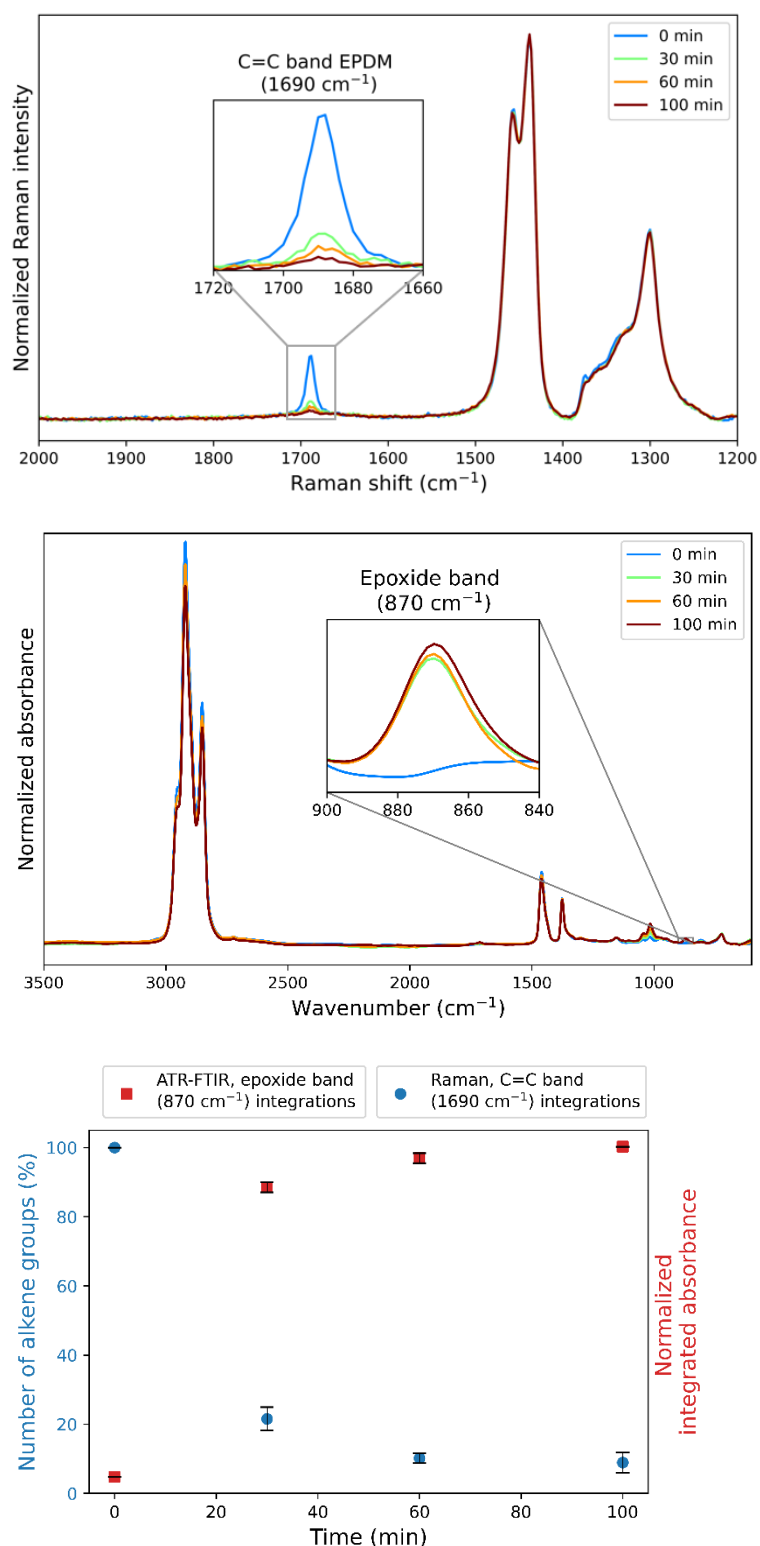


Figure S8. Top: Raman spectra (λ_{exc} 785 nm) of EPDM rubber during epoxidation obtained following flash quenching at indicated reaction times, with expansion of the region around the alkene stretching band of the **ENB** unit at 1690 cm⁻¹. Middle: ATR-FTIR spectra of the same samples with expansion of the region around the epoxide band at 870 cm⁻¹. Bottom: Integration of Raman band at 1690 cm⁻¹ and FTIR absorption at 870 cm⁻¹ with time, with standard deviation of repeated measurements on each sample. Conditions: EPDM rubber (15 mM in alkene), 0.3 mM Mn(II)(ClO₄)₂·6H₂O, 1.5 mM sodium picolinate, 60 mM butanedione, 30 mM acetic acid, 300 mM H₂O₂ in cyclohexane/cyclohexanone (50/50 v/v) at 50 °C. Samples were withdrawn and quenched in acetone at the specified times.

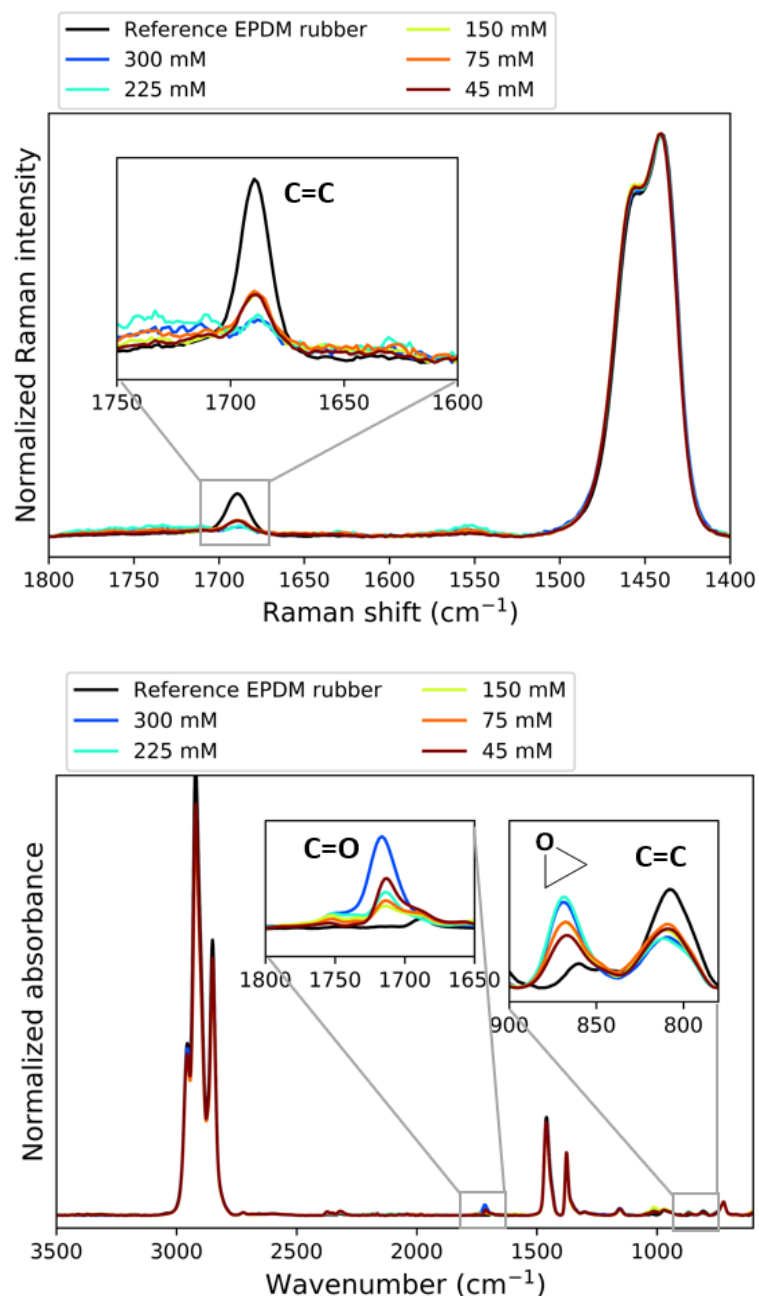


Figure S9. Raman spectra (recorded at 785 nm with a BX51 upright microscope) (top) and ATR-FTIR spectra (bottom) recorded after epoxidation of EPDM rubber with various concentrations of butanedione (300, 225, 150, 75 and 45 mM) after 2 h stirring. Conditions: EPDM rubber (30 mM in alkene), 0.3 mM Mn(II)(ClO₄)₂·6H₂O, 1.5 mM sodium picolinate, 30 mM acetic acid and 10 equivalents of H₂O₂ (50%, aq.) in 50/50 wt% cyclohexane/cyclohexanone.

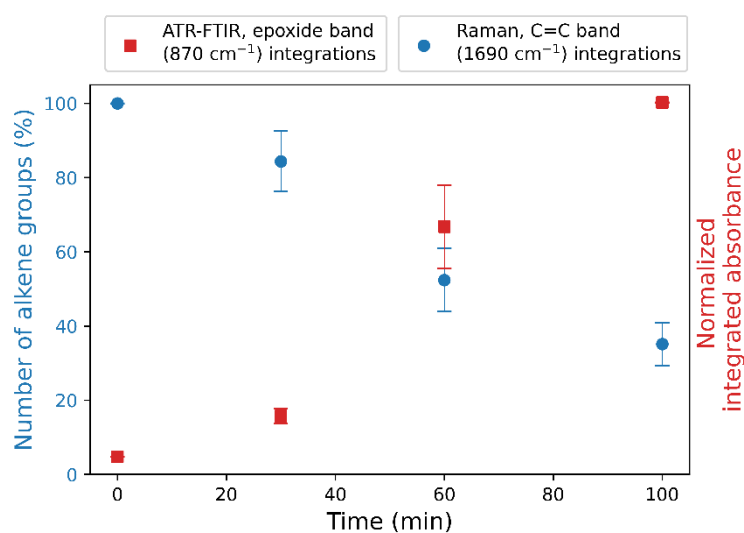
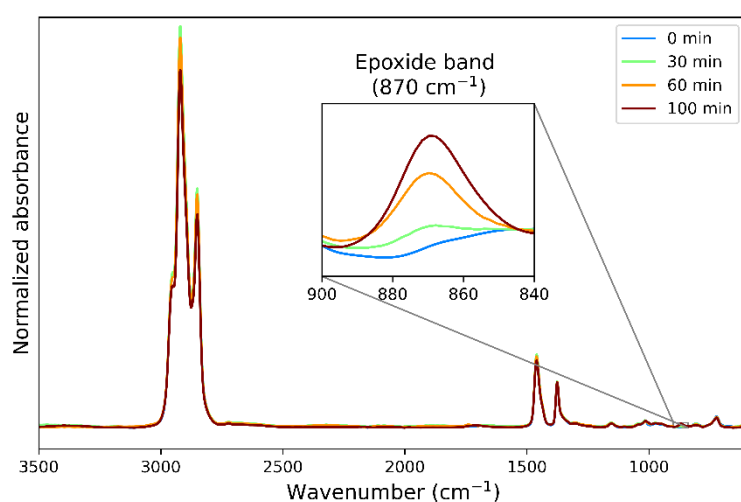
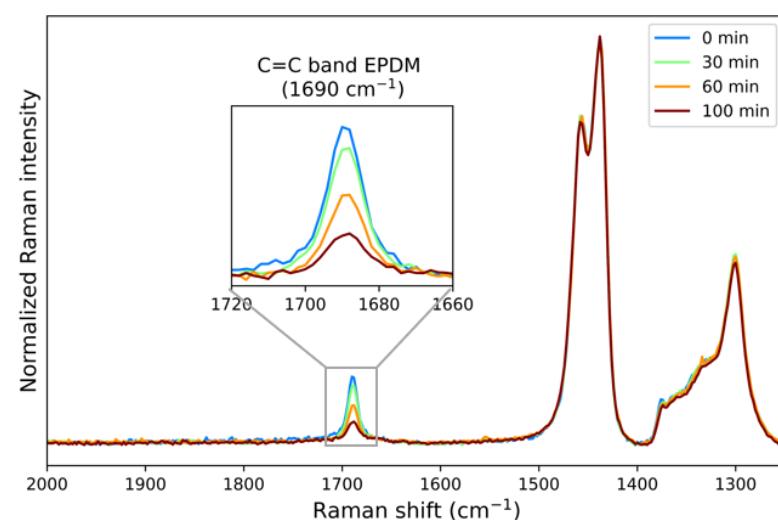


Figure S10. Top: Raman spectra (λ_{exc} 785 nm) of EPDM rubber during epoxidation obtained following flash quenching at indicated reaction times, with expansion of the region around the alkene stretching band of the ENB unit at 1690 cm^{-1} . Middle: ATR-FTIR spectra of the same samples with expansion of

the region around the epoxide band at 870 cm^{-1} . Bottom: Integration of Raman band at 1690 cm^{-1} and FTIR absorption at 870 cm^{-1} with time, with standard deviation of repeated measurements on each sample. Conditions: EPDM rubber (30 mM in alkene), $0.3\text{ mM Mn(II)(ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, 1.5 mM sodium picolinate, 30 mM acetic acid, $300\text{ mM H}_2\text{O}_2$ in cyclohexane/cyclohexanone (50/50 v/v) at $50\text{ }^\circ\text{C}$. Samples were withdrawn and quenched in acetone at the specified times.

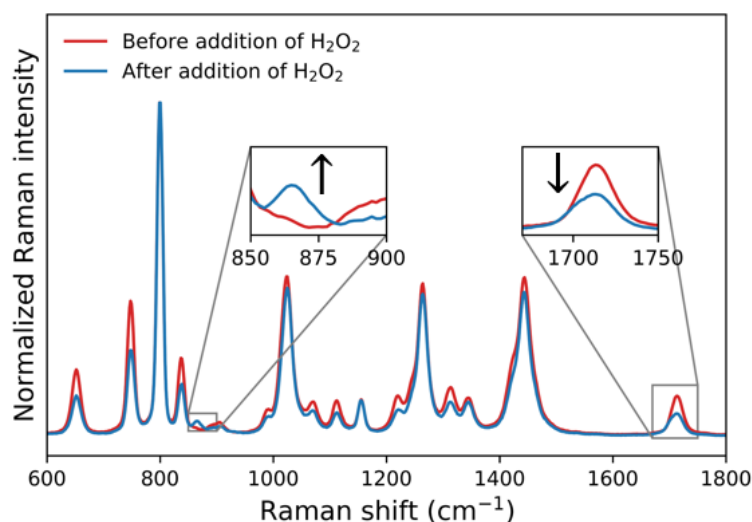


Figure S11. Formation of a hydroperoxy-adduct from cyclohexanone and hydrogen peroxide. Multiple bands of the cyclohexanone come down after hydrogen peroxide is added, but most important is the C=O stretching vibration band at 1720 cm^{-1} of the cyclohexanone that goes down. Around 860 cm^{-1} and band of the hydroperoxy-adduct comes up, originating from the O-O stretching vibration. Conditions: 4 M cyclohexanone and $2\text{ M H}_2\text{O}_2$ (50%, aq.) in cyclohexane. The spectra are normalized on the band at 800 cm^{-1} of cyclohexane.

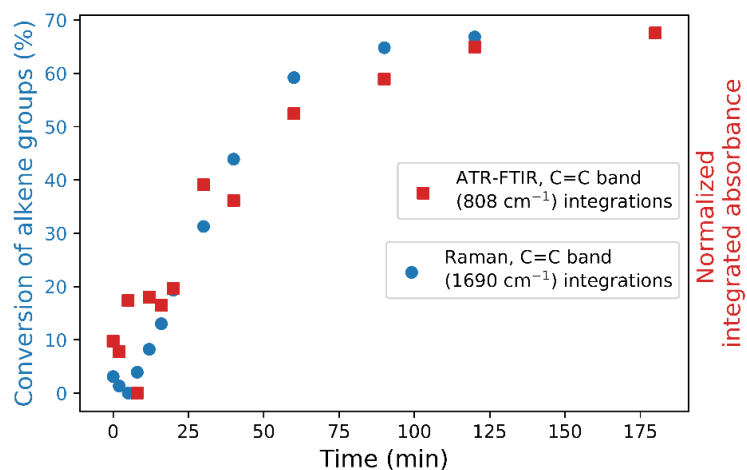


Figure S12. Integration of the alkene stretching band at 808 cm⁻¹ from the ATR-FTIR spectra compared to the integrations of the alkene band at 1690 cm⁻¹ from the Raman spectra. The Raman integrations give a more accurate representation than the ATR-FTIR integrations. Conditions: EPDM rubber (30 mM in alkene), 0.3 mM Mn(II)(ClO₄)₂·6H₂O, 1.5 mM sodium picolinate, 60 mM butanedione, 30 mM acetic acid, 10 equiv. H₂O₂ in cyclohexane/cyclohexanone (50/50) at 50 °C.