Supporting Information Part B Analysis Methods and Raw Data)

Mechanism of Cobalt-Catalyzed Heterodimerization of Acrylates and 1,3-Dienes. A Potential Role of Cationic Cobalt(I) Intermediates

IR Analysis

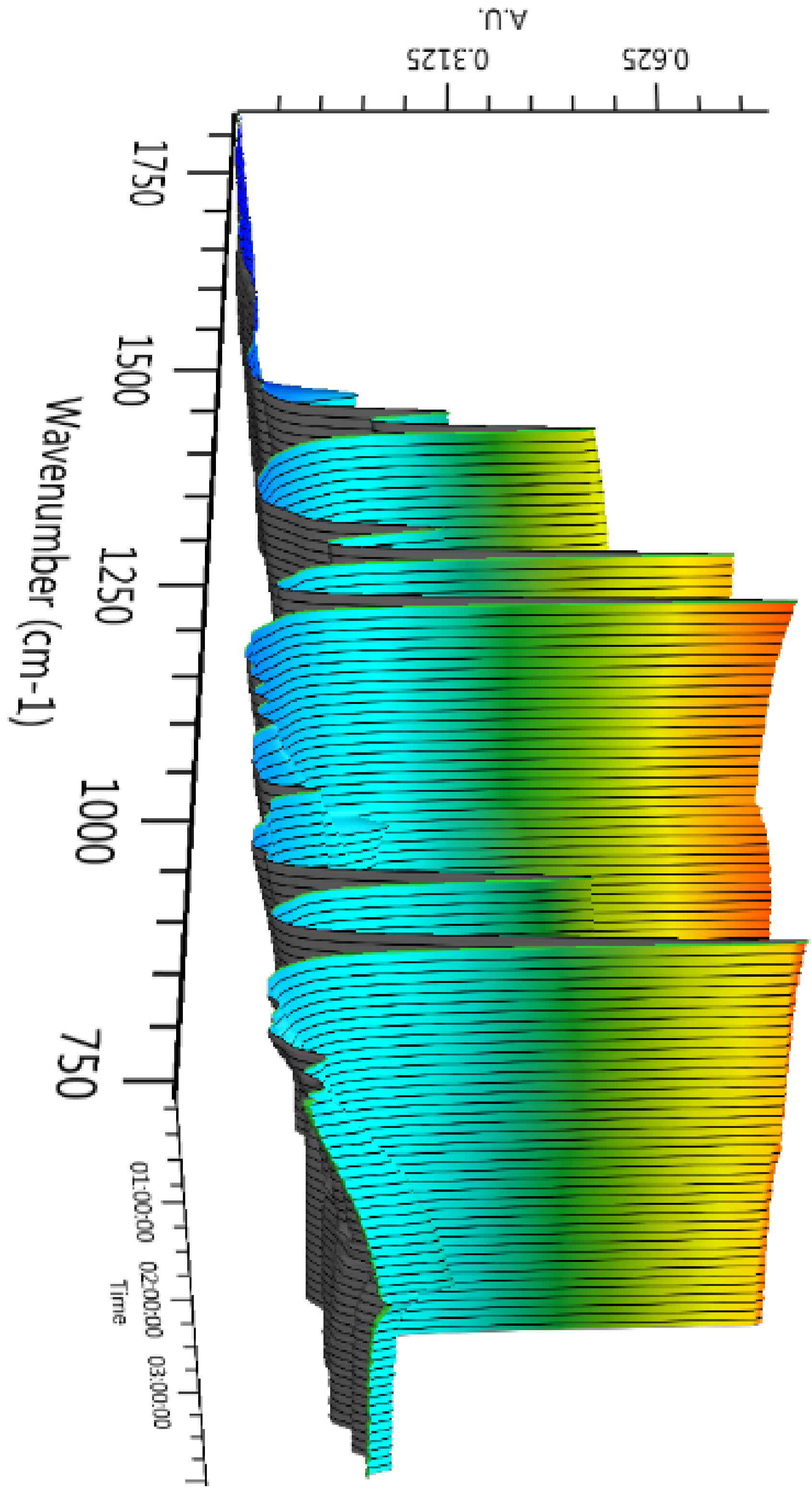
A ReactIR probe was used to collect in-situ data on the reaction progress and provided an infrared spectrum every 30 sec, recording the wavenumbers from 3000 cm^{-1} to 650 cm^{-1}. The peaks that are monitored for this reaction are as follows: for the methyl acrylate, 1401 cm^{-1}, for the 2,3-dimethyl-1,3-butadiene, 887 cm^{-1}.[4] Initially, the reaction mixture was prepared as described in Section 4.1.3. Before adding the substrates, the ReactIR data collection was started to ensure that the analysis would capture the initial reaction. After injecting the substrates, the data were collected for two hours. After recording the data, the data were converted to an excel file that could be analyzed (see below) using a MATLAB script (see SI). The MATLAB script imported the data into a matrix, extracting the time into a separate variable. Time values were converted from days to hours to facilitate analysis.

From the matrix of FTIR absorption, the absorption values associated with each compound were extracted into separate vectors using a multi-step process. While the absorption intensity at the specified wavelength for a compound could be used to determine the concentration of that compound, it was found that deconvoluting the FTIR spectra resulted in production rates that fit first order kinetics. Indeed, directly using the FTIR absorption intensity deviated from first order. The deconvolution procedure involved fitting the FTIR spectra in the range of 880 cm^{-1} to 793 cm-1 using seven Gaussians at wavelengths of 881 cm^{-1}, 878 cm^{-1}, 811 cm^{-1}, 810 cm^{-1}, 851 cm^{-1}, 887 cm^{-1}, and 885 cm^{-1}.The peaks at 887 cm^{-1} and 885 cm^{-1} were associated with the diene. From this fitting procedure, the program extracts the intensity of the peak over time. A similar procedure was used for the acrylate using peaks at 1402 cm^{-1}, 1429 cm^{-1}, 1450 cm^{-1}, 1436 cm^{-1}, and 1421 cm^{-1} with the peak at 1402 cm^{-1} being associated with the acrylate.

For the data after substrate injection, the data were processed using the MATLAB function smooth, using the 'rlowess' method. The MATLAB script then converted the smoothed absorption data to concentration. The absorption values after the injection (concentration expected from mixing substrates into the solvent) and at the end of reaction (concentration determined based on yield calculated from GC analysis of reaction mixture) compared favorably with absorption values expected calibration standards.

This data was further fit using the polyfit function in MATLAB to a 4^{th} or 5^{th} order polynomial. The derivative was calculated of these coefficients using the function polyder to give the reaction rate. This method was used for all trials, including same excess, different excess, and catalyst loading analysis

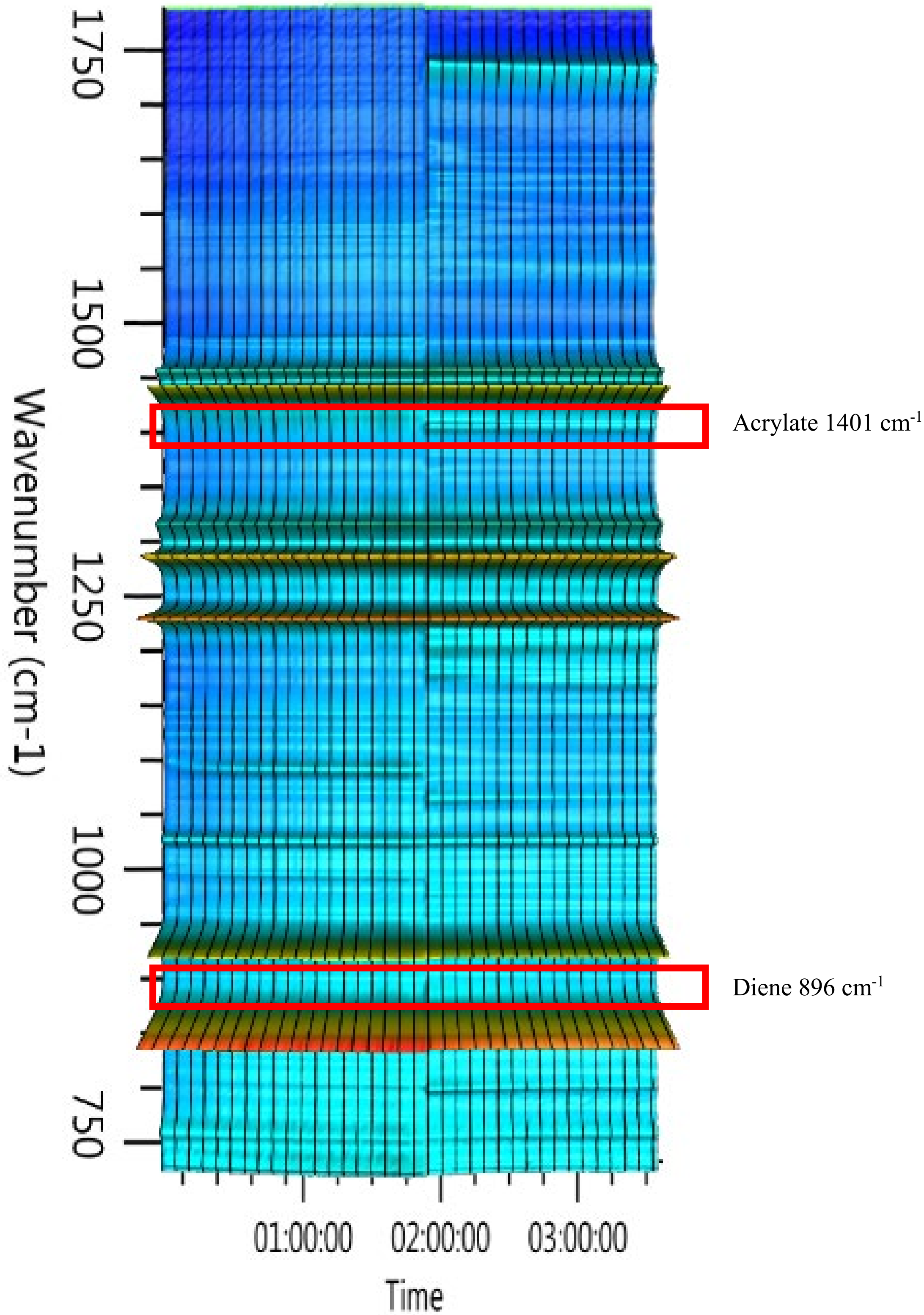
3D Plot



0.31 M Acrylate, 0.15 M Diene, 0.152 mmol DPPCoBr$_2$, 1.52 mmol Zn, 1.57 mmol ZnBr$_2$. 98% Conversion. Surface from ReactIR software.

Figure SS1: An isomeric view of the prototypical unprocessed IR spectrum (0.31 M acrylate, 0.15 M diene, 0.152 mmol $DPPPCoBr_2$, 1.52 mmol Zn, 1.57 mmol $ZnBr_2$) spanning the four hours of the reaction. Because of the nature of the probe, a clean spectrum could only be obtained from ca. 750 cm^{-1} to ca. 1750 cm^{-1}. Blue represents a low intensity and orange represents a high intensity. All other intensities are represented by this color scale (blue to orange is equivalent to low intensity to high intensity).

2D Surface



0.31 M Acrylate, 0.15 M Diene, 0.152 mmol $DPPCoBr_2$, 1.52 mmol Zn, 1.57 mmol $ZnBr_2$. 98% Conversion. Surface from ReactIR software.

Figure SS2: An aerial view of the prototypical unprocessed IR spectrum (0.31 M acrylate, 0.15 M diene, 0.152 mmol $DPPPCoBr_2$, 1.52 mmol Zn, 1.57 mmol $ZnBr_2$). The y-axis represents the wavelength (750 cm^{-1} to 1750 cm^{-1}). The x-axis represents the time of the reaction (0 hr to 4 hr). The z-axis (not shown) represents the intensity of the peaks. The intensity is represented by color, where orange is the highest intensity and dark blue is the lowest intensity. The peaks highlighted in red represent the cm^{-1} of the starting material. 1401 cm^{-1} is the acrylate peak monitored throughout the reaction. 896 cm^{-1} is the diene peak that is monitored throughout the reaction.

Intensity vs cm^{-1} Acrylate

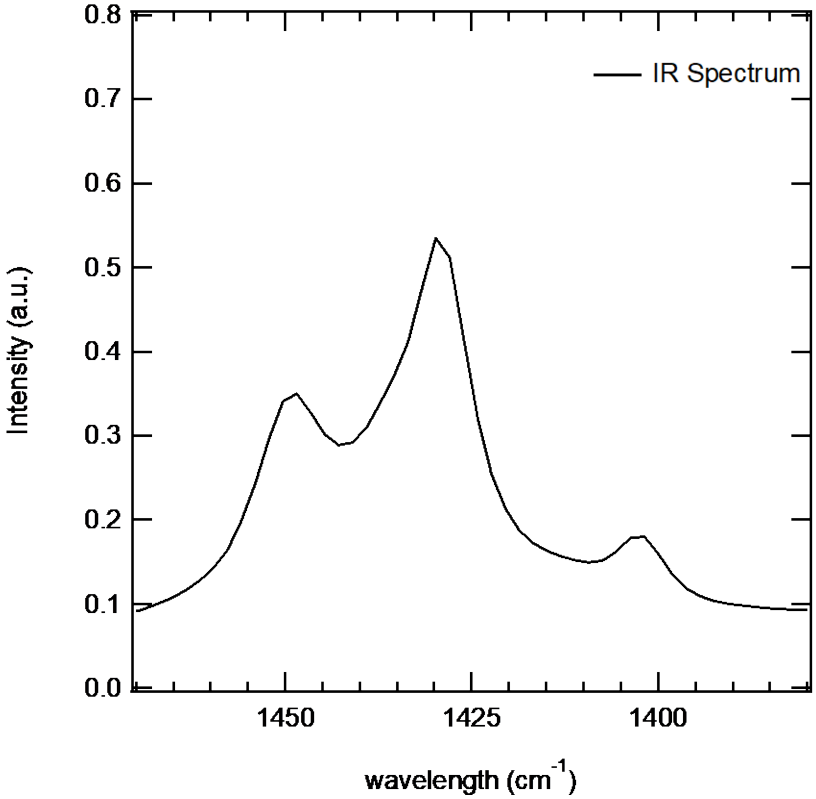


Figure SS3: The IR spectrum with intensity on the y-axis and wavelength on the x-axis localized on the peak for the acrylate, 1402 cm^{-1}. The other, high intensity peaks, are from the solvent DCE. This spectrum is taken at the highest intensity for the peak at 1402 cm^{-1} directly after the addition of the starting materials to the catalyst (at two hours from Figure 1 and 2).

Deconvolution for Acrylate Peaks

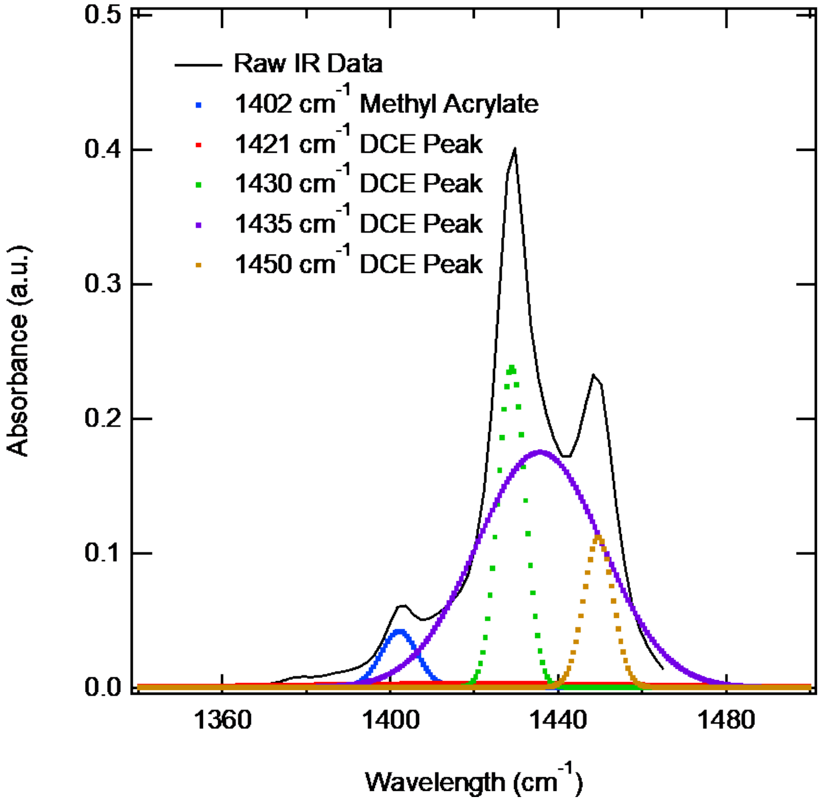


Figure SS4: The deconvolution process for the experimental data. The blue line represents the experimental data. The dashed colored lines represent different Gaussians that were calculated to best fit the data. The dark blue dashed line is the calculated Gaussian for the peak at 1402 cm^{-1}. This is the characteristic peak for the acrylate.

Intensity vs cm^{-1} Diene

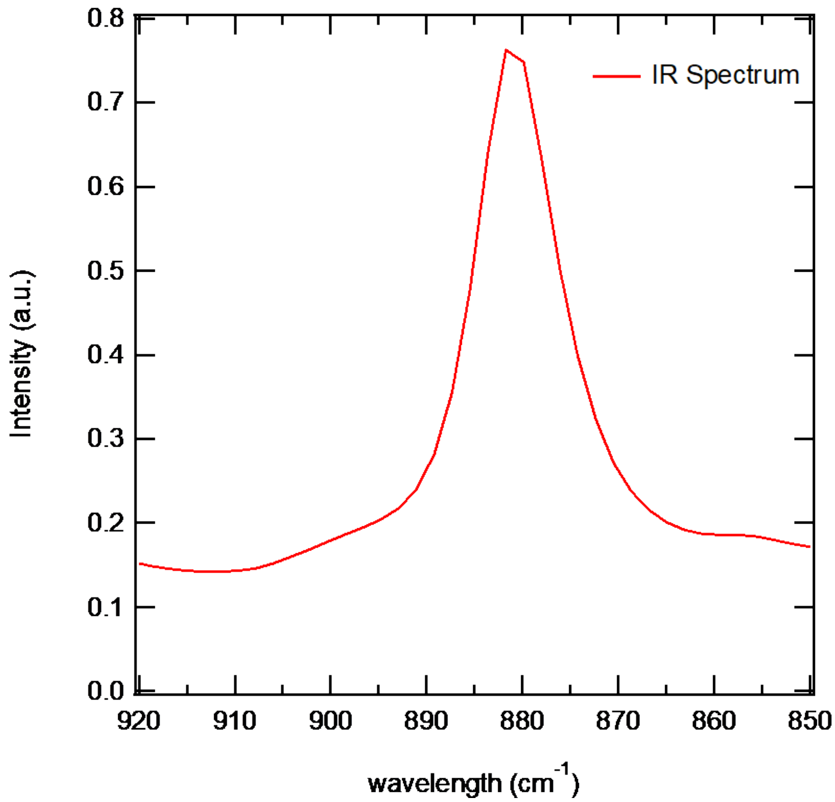


Figure SS5: The IR spectrum with intensity on the y-axis and wavelength on the x-axis localized on the peak for the diene, 896 cm^{-1} (The shoulder off of the large peak at ca. 880 cm^{-1}). The other, high intensity peak, is from the solvent DCE. This spectrum is taken at the highest intensity for the peak at 896 cm^{-1} directly after the addition of the starting materials to the catalyst (at two hours from Figure 1 and 2).

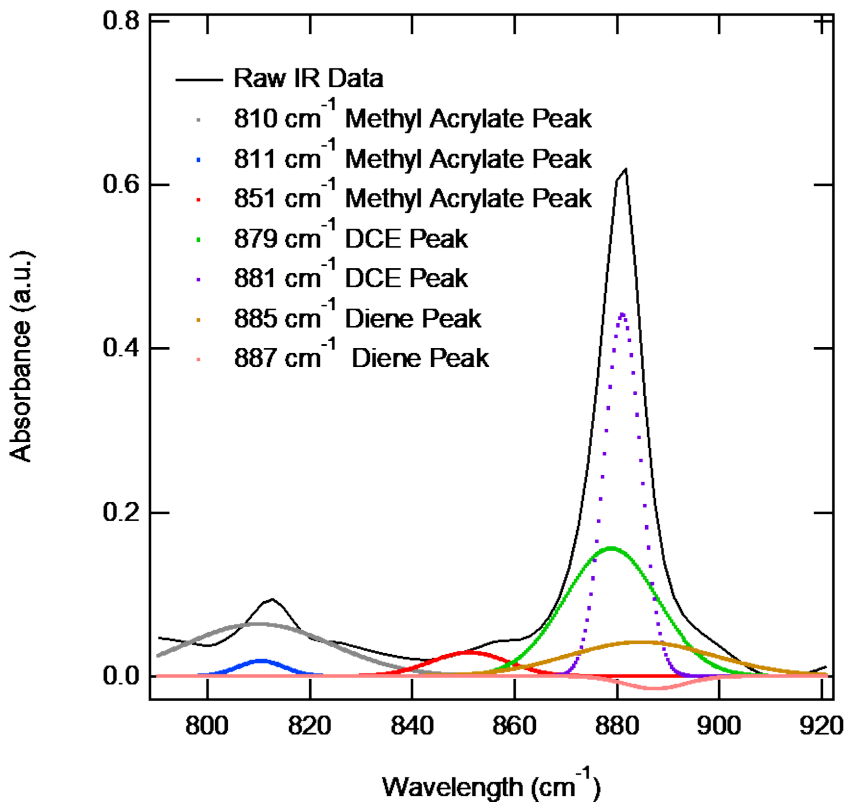


Figure SS6: The deconvolution process for the experimental data. The black line represents the experimental data. The dashed colored lines represent different Gaussians that were calculated to best fit the data. The peach and the orange dashed line is the calculated Gaussian for the peak at 1402 cm^{-1}. This is the characteristic peak for the acrylate.

Intensity vs cm^{-1} Acrylate

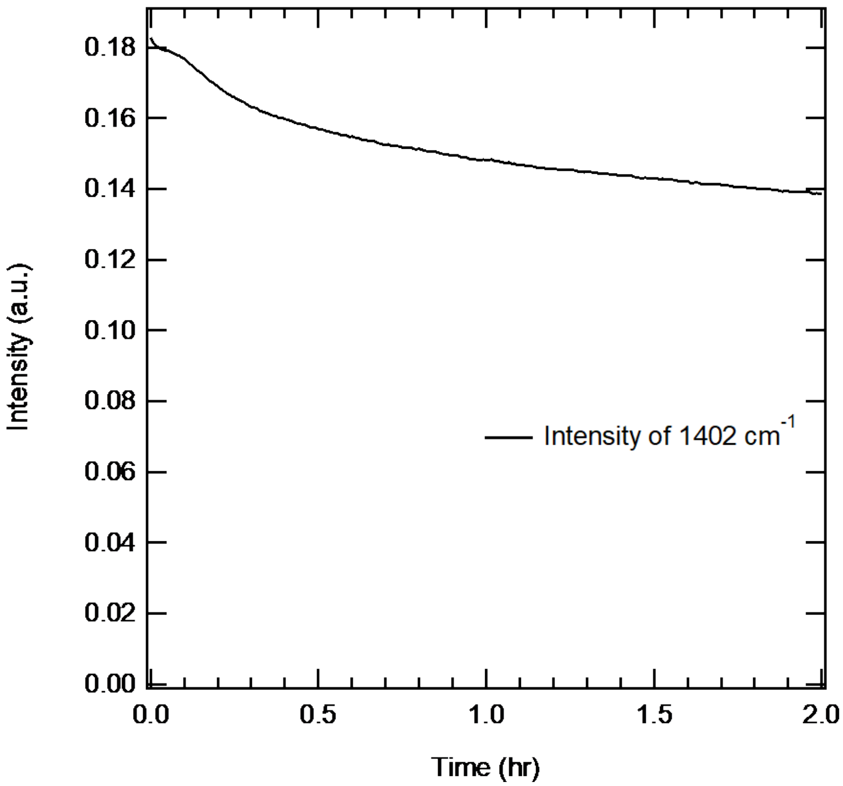


Figure SS7: The intensity at 1402 cm^{-1} measured across the time of the reaction from Figure 1 and 2. Intensity is graphed on the y axis and time is graphed on the x-axis. Time zero is at the time of injection (after a two hours stir time two hours with the precatalyst, reducing agent, and activator). After reacting for two hours the reaction was stopped and monitoring ended.

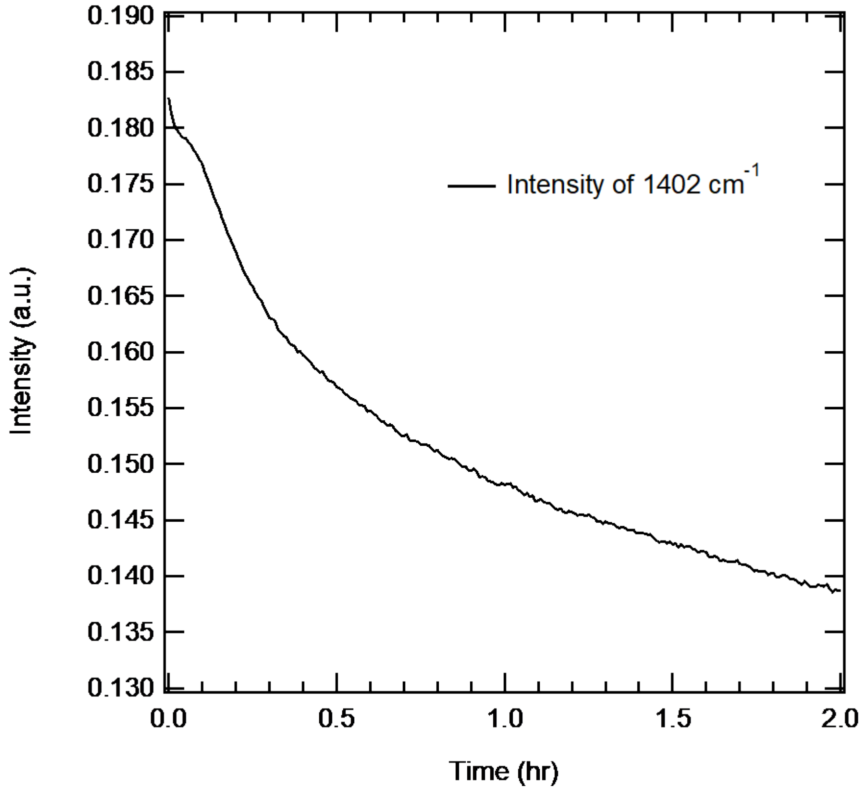


Figure SS8: Zoomed in version of Figure 7. The intensity at 1402 cm^{-1} measured across the time of the reaction from Figure 1 and 2. Intensity is graphed on the y axis and time is graphed on the x-axis. Time zero is at the time of injection (after a two hours stir time two hours with the precatalyst, reducing agent, and activator). After reacting for two hours the reaction was stopped and monitoring ended.

Intensity vs cm^{-1} Diene

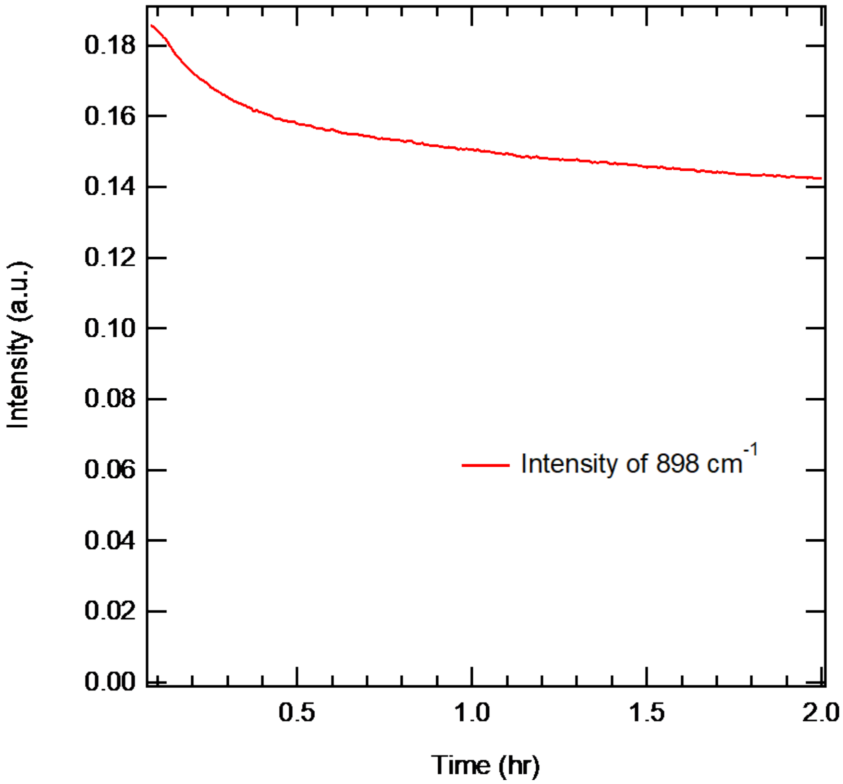


Figure SS9: The intensity at 896 cm^{-1} measured across the time of the reaction from Figure 1 and 2. Intensity is graphed on the y axis and time is graphed on the x-axis. Time zero is at the time of injection (after a two hours stir time two hours with the precatalyst, reducing agent, and activator). After reacting for two hours the reaction was stopped and monitoring ended.

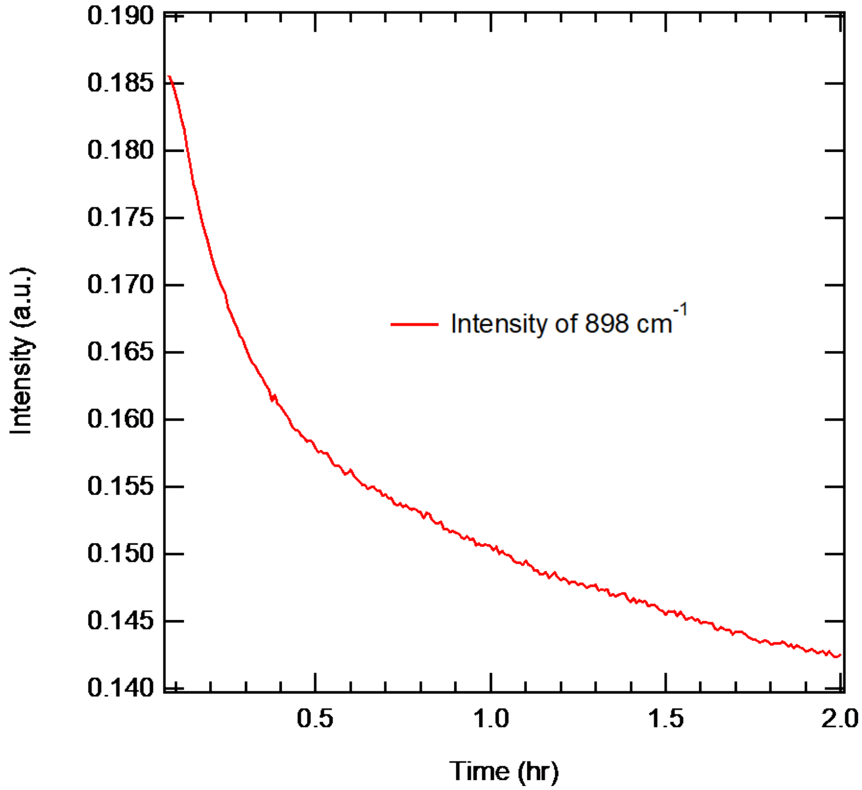


Figure SS10: Zoomed in version of Figure 9. The intensity at 896 cm^{-1} measured across the time of the reaction from Figure 1 and 2. Intensity is graphed on the y axis and time is graphed on the x-axis. Time zero is at the time of injection (after a two hours stir time two hours with the precatalyst, reducing agent, and activator). After reacting for two hours the reaction was stopped and monitoring ended.

Concentration vs Time Acrylate

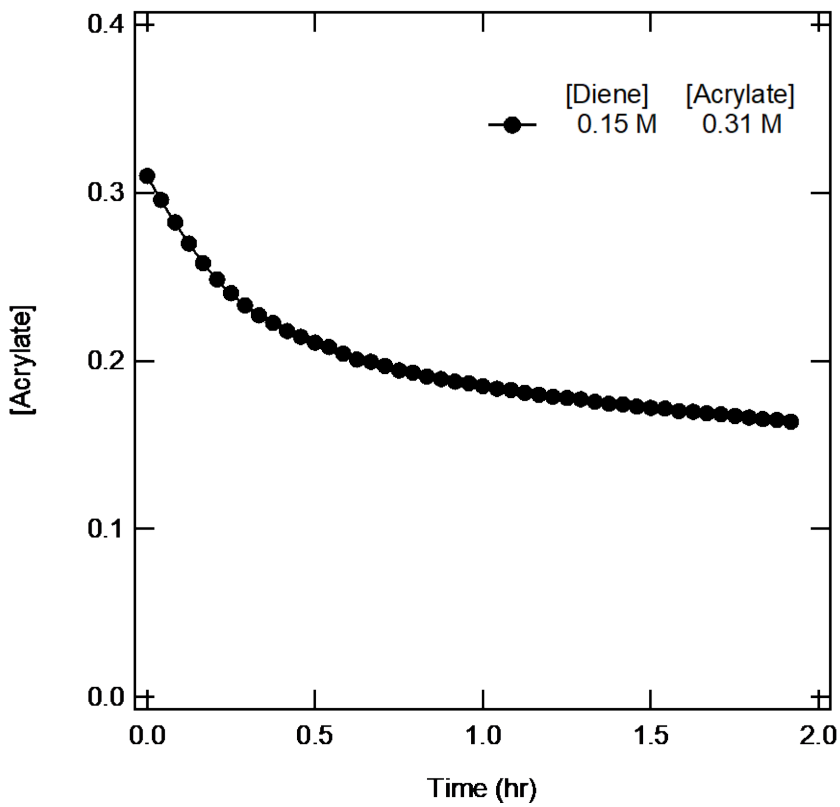


Figure SS11: The concentration vs time curve of acrylate obtained from the intensity vs time curve in Figure 7 and 8. The concentration is on the y-axis and the time is on the x-axis. Time zero is at the time of addition of the acrylate and time two hours is when the reaction was stopped.

Concentration vs Time Acrylate Deconvoluted

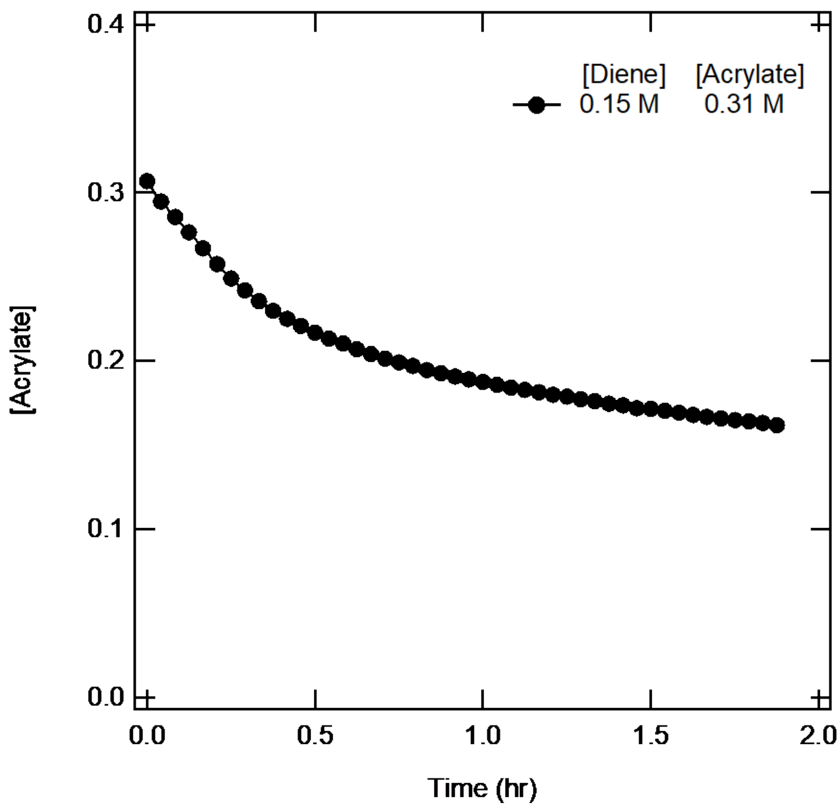


Figure SS12: The deconvoluted concentration vs time curve of acrylate obtained from the concentration vs time curve in Figure 7, 8, and 11. The concentration is on the y-axis and the time is on the x-axis. Time zero is at the time of addition of the acrylate and time two hours is when the reaction was stopped.

Concentration vs Time Diene

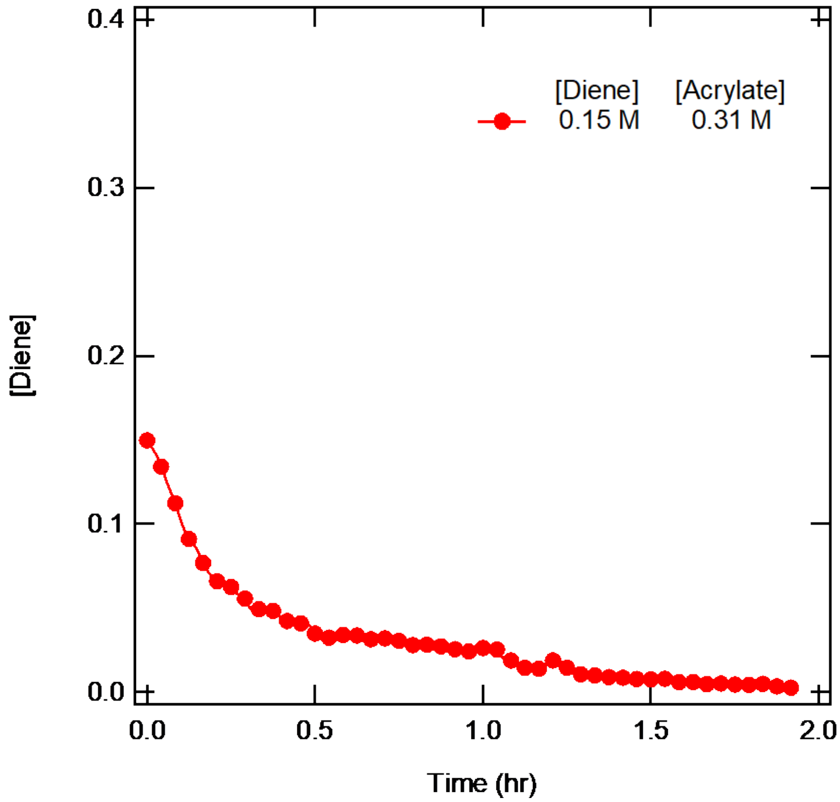


Figure SS13: The concentration vs time curve of diene obtained from the intensity vs time curve in Figure 9 and 10. The concentration is on the y-axis and the time is on the x-axis. Time zero is at the time of addition of the diene and time two hours is when the reaction was stopped.

Concentration vs Time Diene Deconvoluted

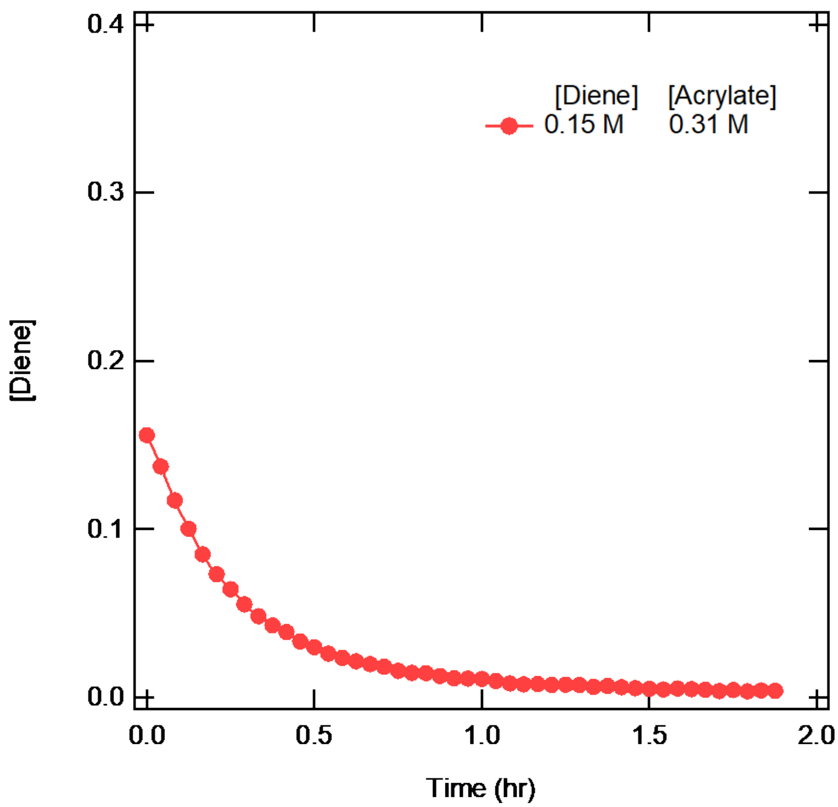


Figure SS14: The deconvoluted concentration vs time curve of diene obtained from the concentration vs time curve in Figure 9, 10, and 13. The concentration is on the y-axis and the time is on the x-axis. Time zero is at the time of addition of the diene and time two hours is when the reaction was stopped.

Rate of Acrylate vs [Acrylate]

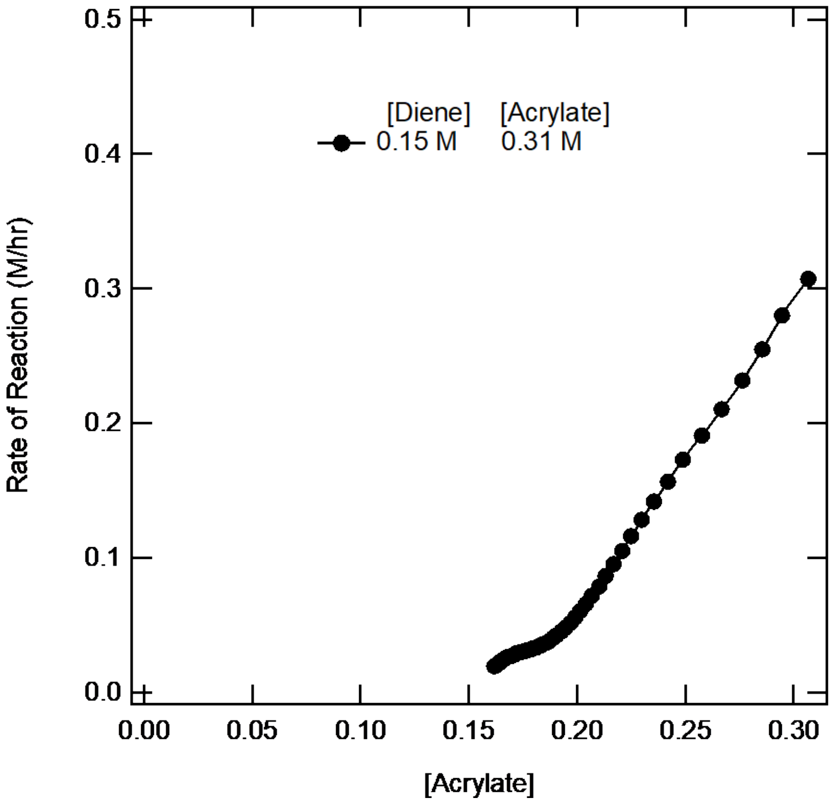


Figure SS15: The rate of acrylate consumption graphed against the concentration of acrylate. Rate of acrylate consumption is on the y-axis and acrylate concentration is on the x-axis. The rate was calculated from the polynomial fit of the deconvoluted concentration of acrylate vs time curve seen in Figure 12.

Rate of Diene vs [Diene]

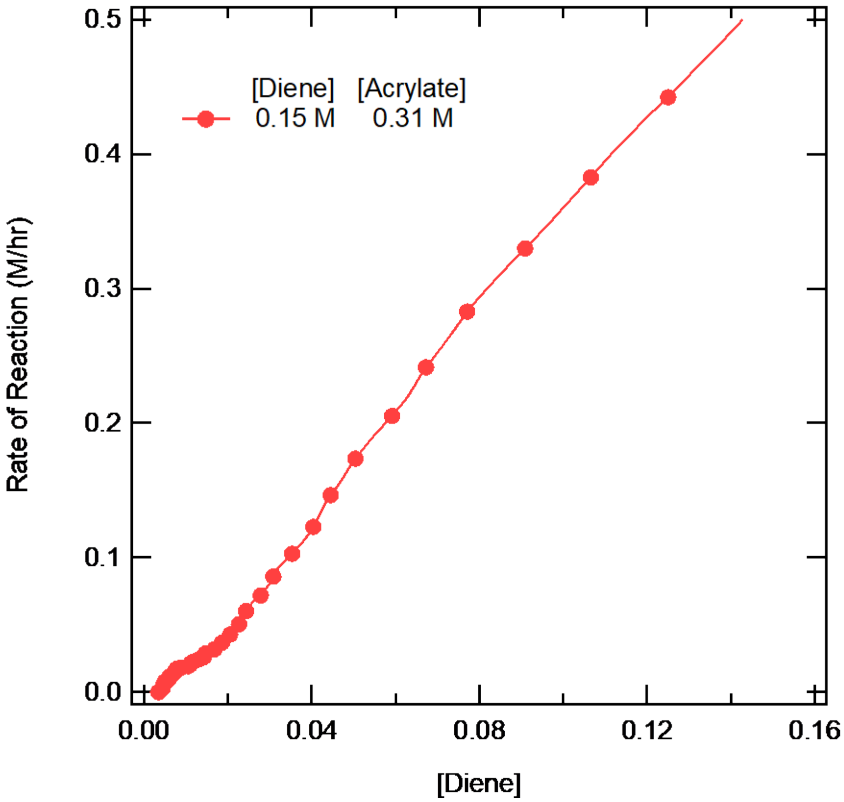


Figure SS16. The rate of diene consumption graphed against the concentration of diene. Rate of diene consumption is on the y-axis and diene concentration is on the x-axis. The rate was calculated from the polynomial fit of the deconvoluted concentration of diene vs time curve seen in Figure 14.

Different Excess Raw Data 0.15 M Diene 0.17 M Acrylate

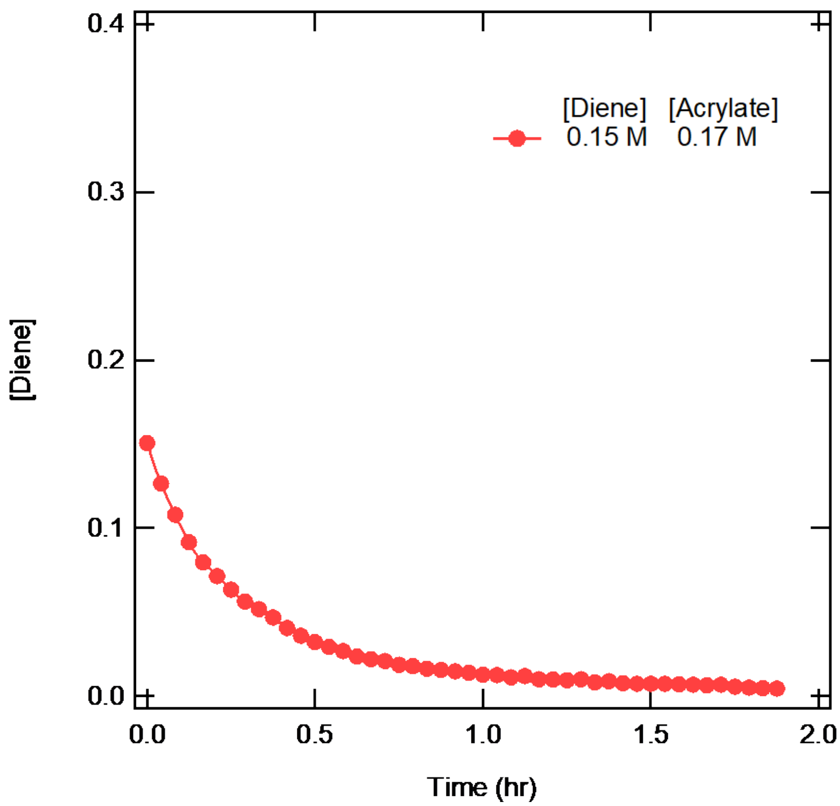


Figure SS17: The diene concentration vs time graph for 0.15 M diene and 0.17 M acrylate. The y-axis is the concentration of diene and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 896 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

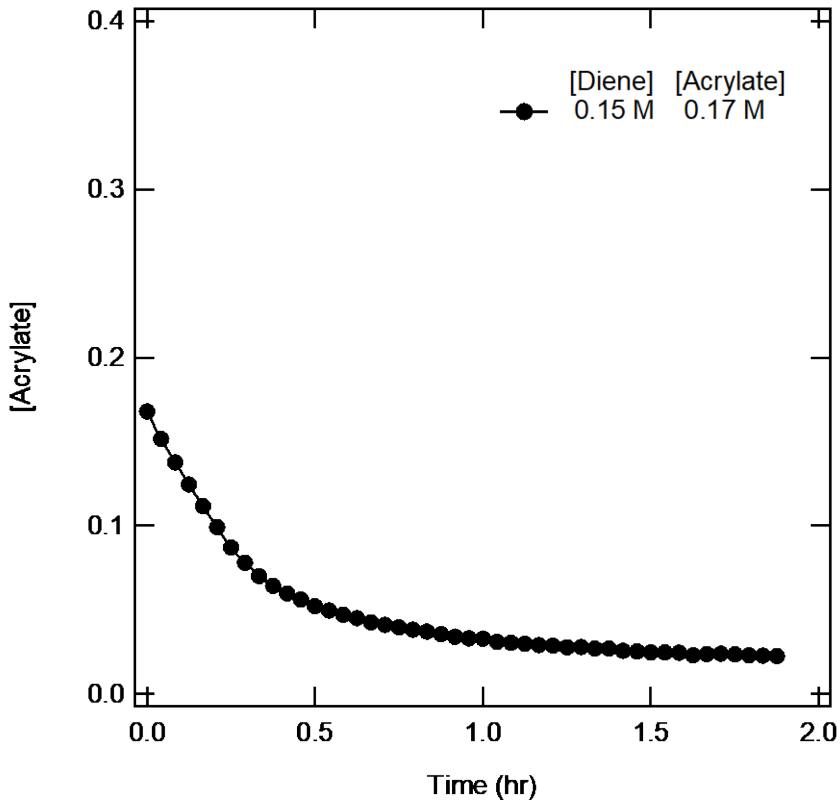


Figure SS18: The acrylate concentration vs time graph for 0.15 M diene and 0.17 M acrylate. The y-axis is the concentration of acrylate and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 1402 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

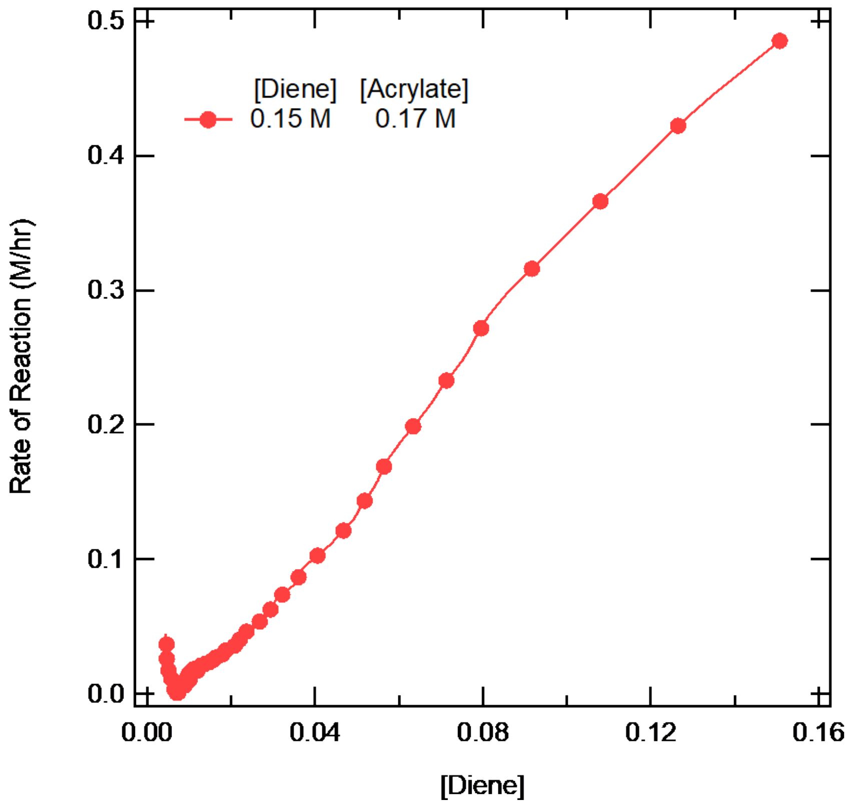


Figure SS19: The rate of diene consumption graphed against the diene concentration. Where rate of diene consumption is on the y-axis and diene concentration is on the x-axis. The rate was calculated from the polynomial fit of the diene concentration vs time graph as seen in Figure 17. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

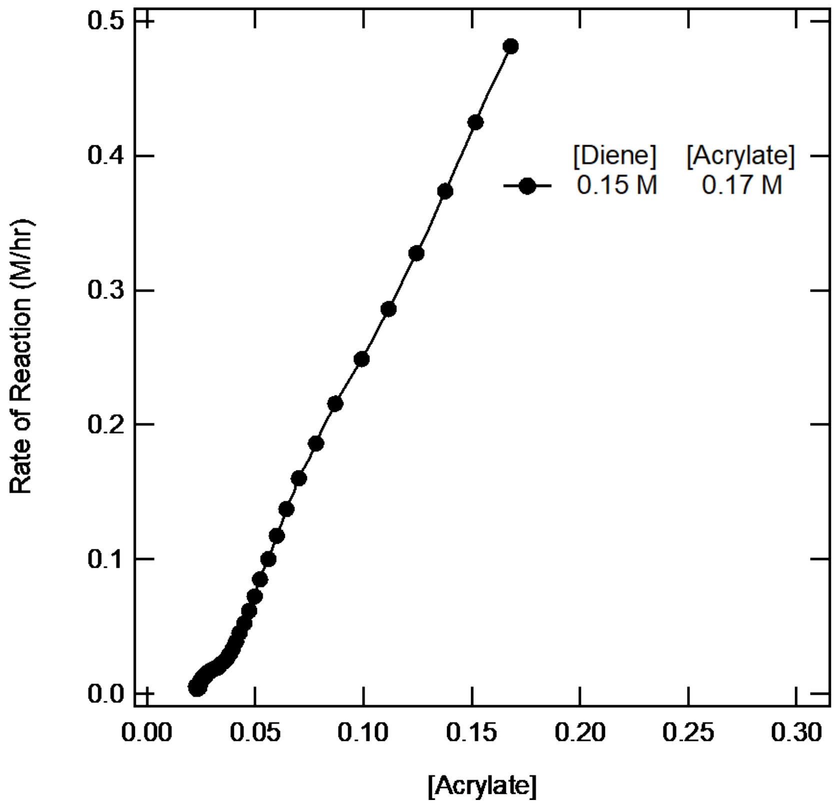


Figure SS20: The rate of acrylate consumption graphed against the acrylate concentration. Where rate of acrylate consumption is on the y-axis and acrylate concentration is on the x-axis. The rate was calculated from the polynomial fit of the acrylate concentration vs time graph as seen in Figure 18. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

0.15 M Diene 0.20 M Acrylate

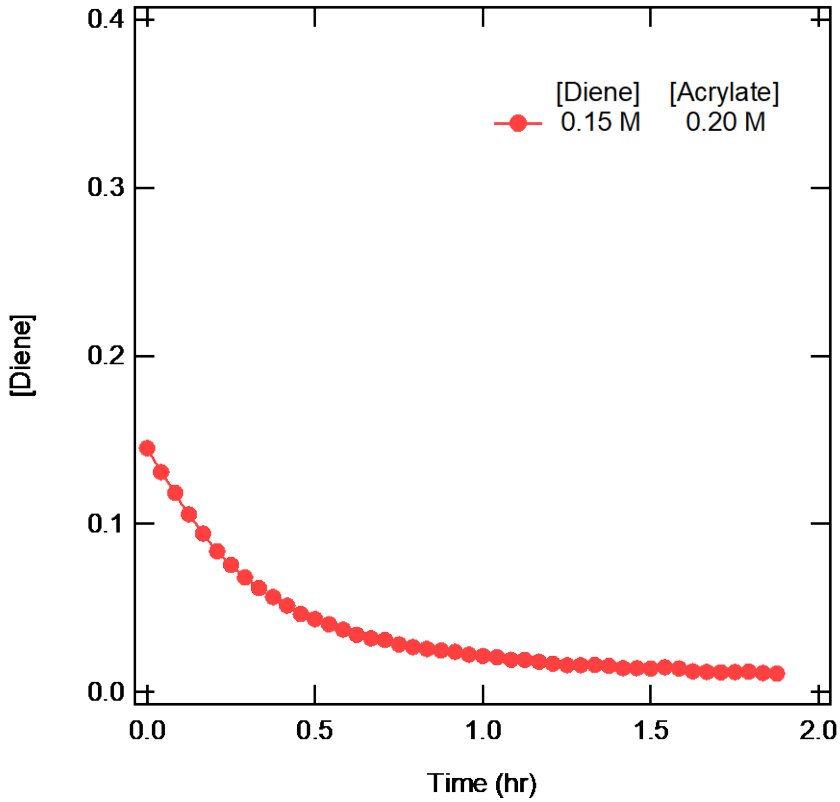


Figure SS21: The diene concentration vs time graph for 0.15 M diene and 0.20 M acrylate. The y-axis is the concentration of diene and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 896 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

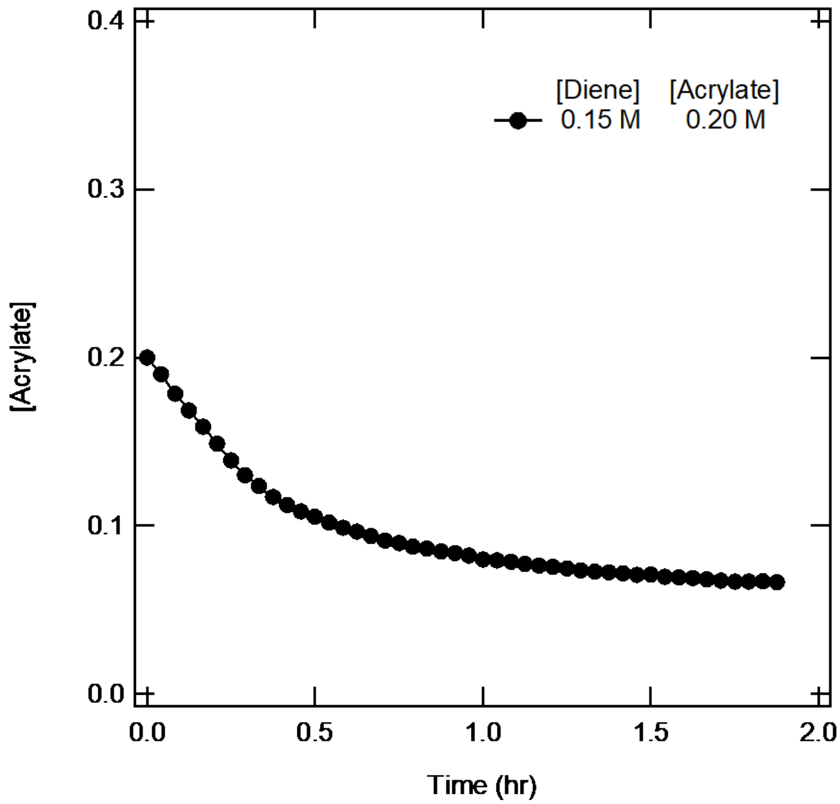


Figure SS22: The acrylate concentration vs time graph for 0.15 M diene and 0.20 M acrylate. The y-axis is the concentration of acrylate and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 1402 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

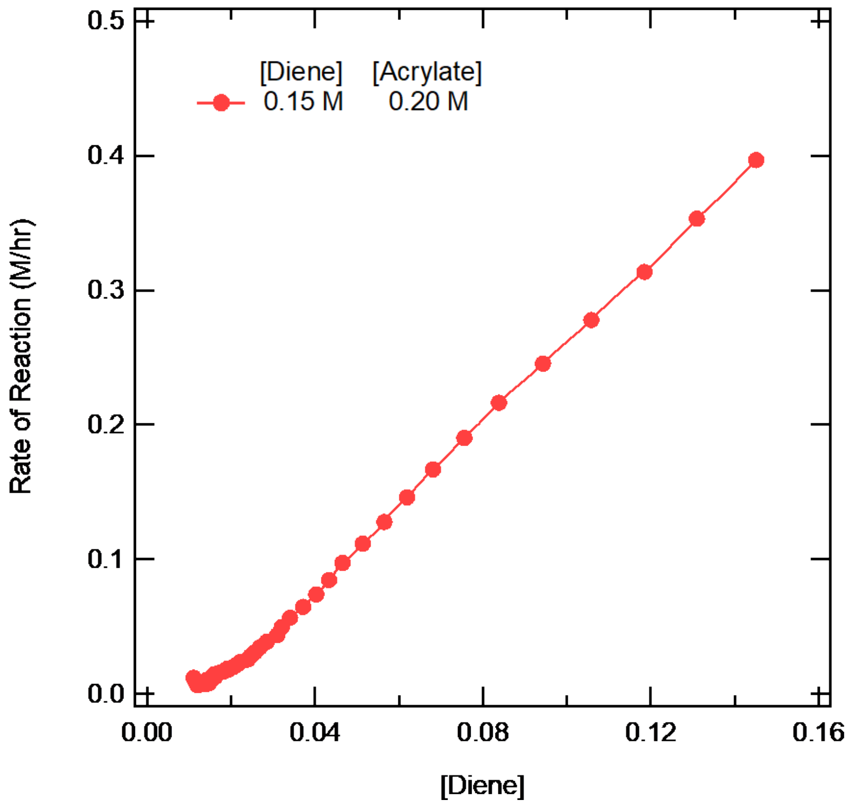


Figure SS23: The rate of diene consumption graphed against the diene concentration. Where rate of diene consumption is on the y-axis and diene concentration is on the x-axis. The rate was calculated from the polynomial fit of the diene concentration vs time graph as seen in Figure 21. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

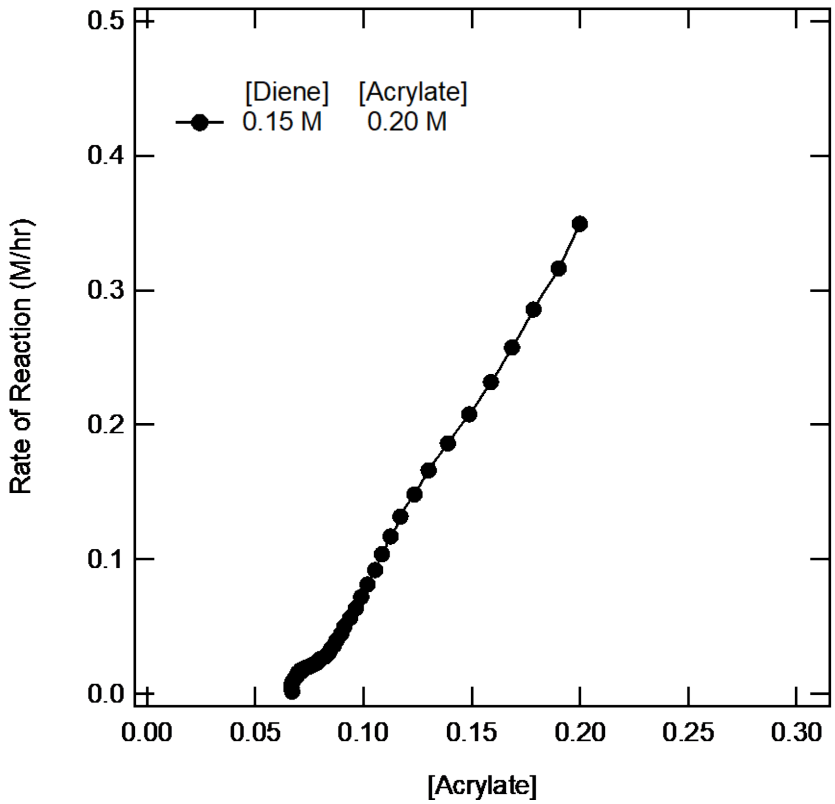


Figure SS24: The rate of acrylate consumption graphed against the acrylate concentration. Where rate of acrylate consumption is on the y-axis and acrylate concentration is on the x-axis. The rate was calculated from the polynomial fit of the acrylate concentration vs time graph as seen in Figure 22. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

0.15 M Diene 0.31 M Acrylate

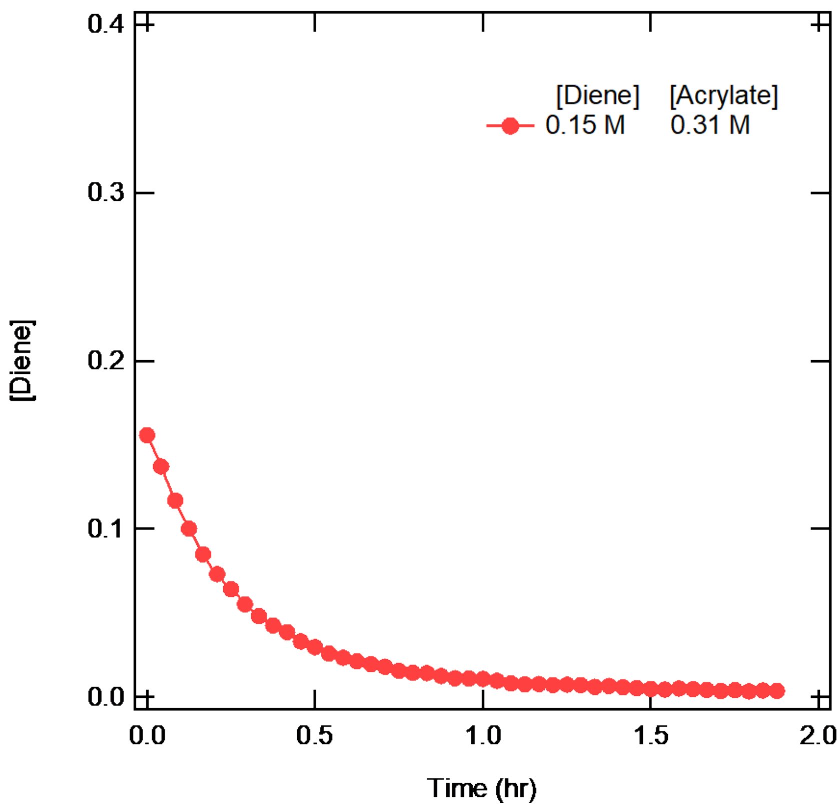


Figure SS25: The diene concentration vs time graph for 0.15 M diene and 0.31 M acrylate. The y-axis is the concentration of diene and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 896 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

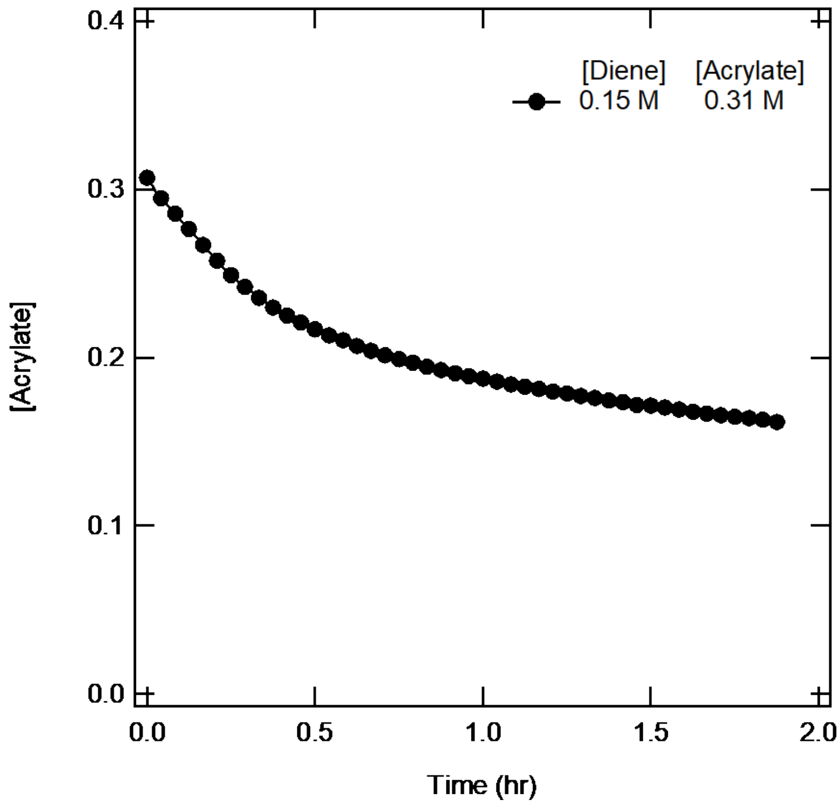


Figure SS26: The acrylate concentration vs time graph for 0.15 M diene and 0.31 M acrylate. The y-axis is the concentration of acrylate and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 1402 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

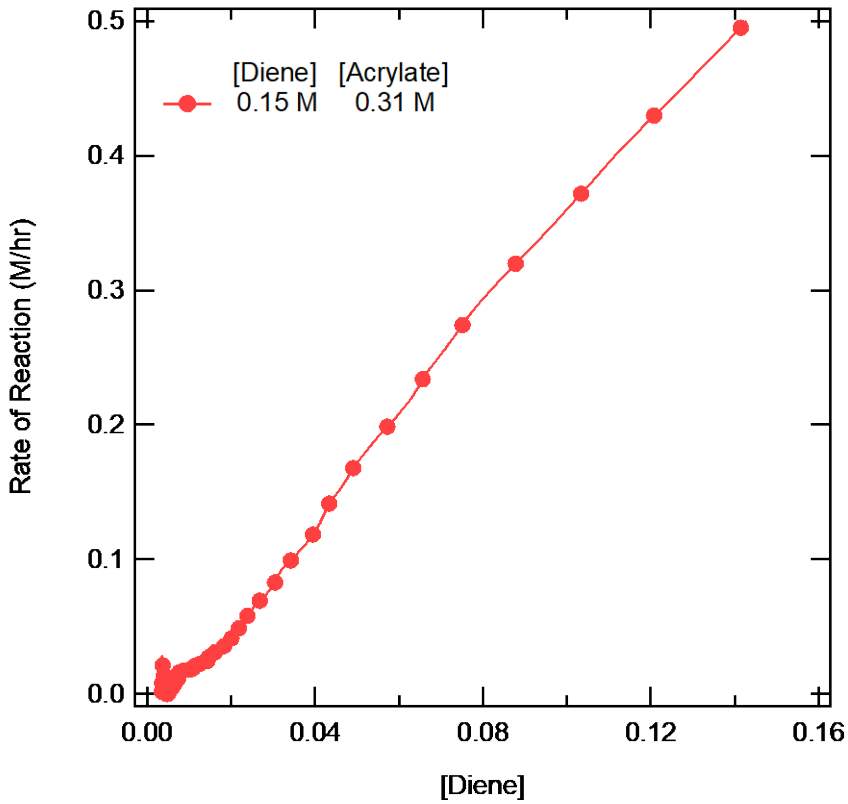


Figure SS27: The rate of diene consumption graphed against the diene concentration. Where rate of diene consumption is on the y-axis and diene concentration is on the x-axis. The rate was calculated from the polynomial fit of the diene concentration vs time graph as seen in Figure 25. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

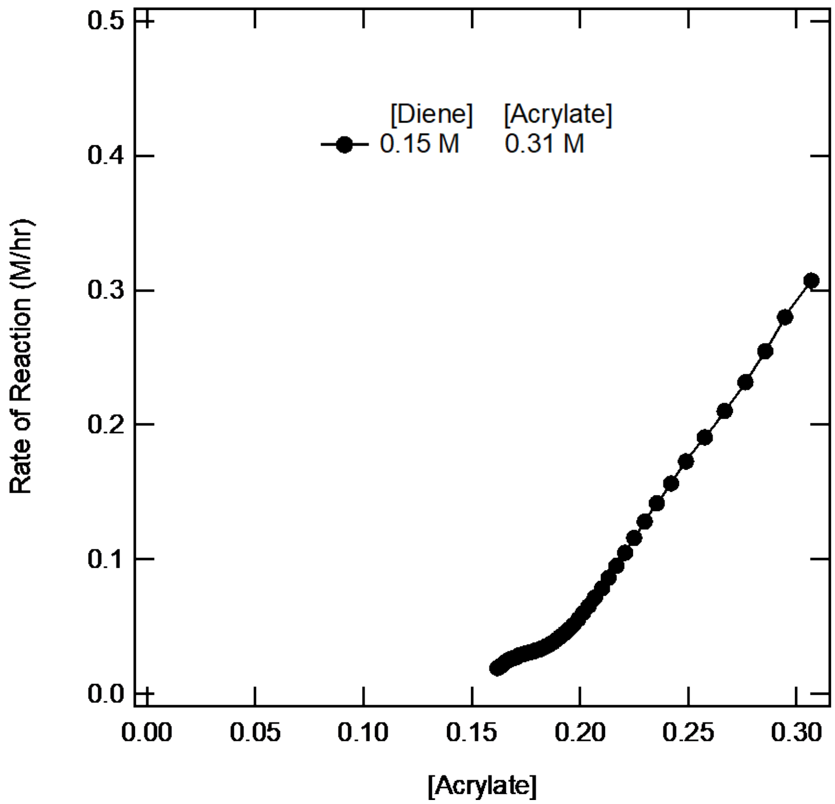


Figure SS28: The rate of acrylate consumption graphed against the acrylate concentration. Where rate of acrylate consumption is on the y-axis and acrylate concentration is on the x-axis. The rate was calculated from the polynomial fit of the acrylate concentration vs time graph as seen in Figure 26. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

0.15 M Diene' 0.31 M Acrylate'

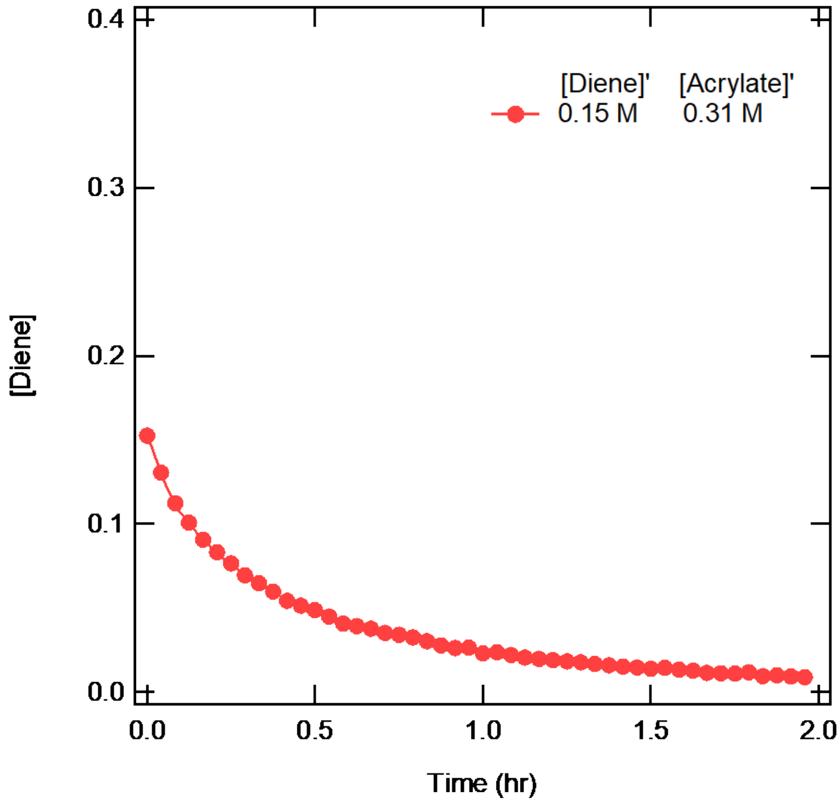


Figure SS29: The diene concentration vs time graph for 0.15 M diene and 0.31 M acrylate. The y-axis is the concentration of diene and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 896 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

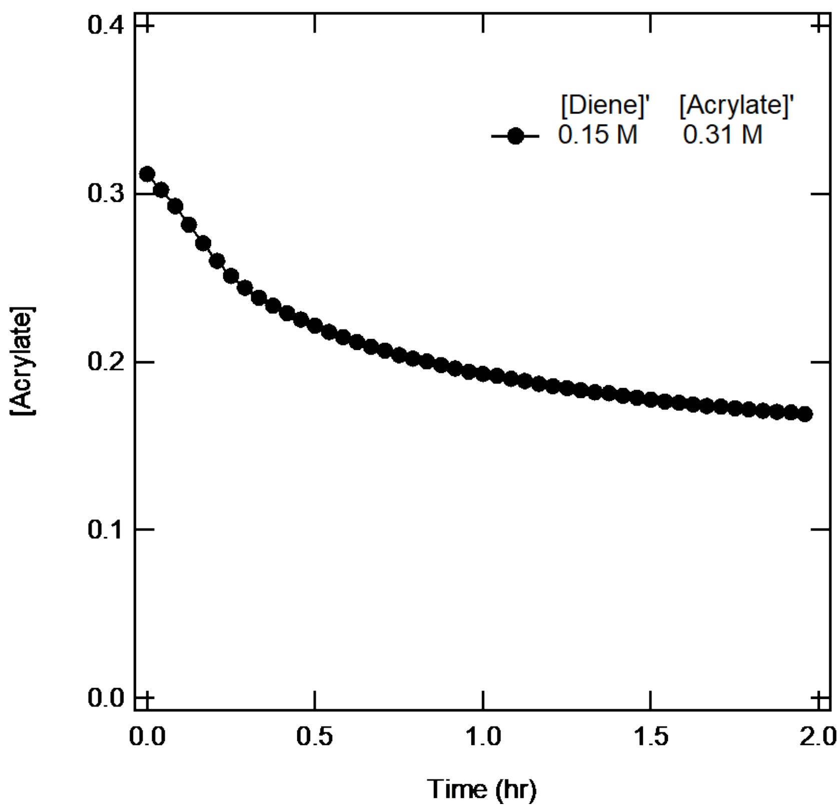


Figure SS30: The acrylate concentration vs time graph for 0.15 M diene and 0.31 M acrylate. The y-axis is the concentration of acrylate and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 1402 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

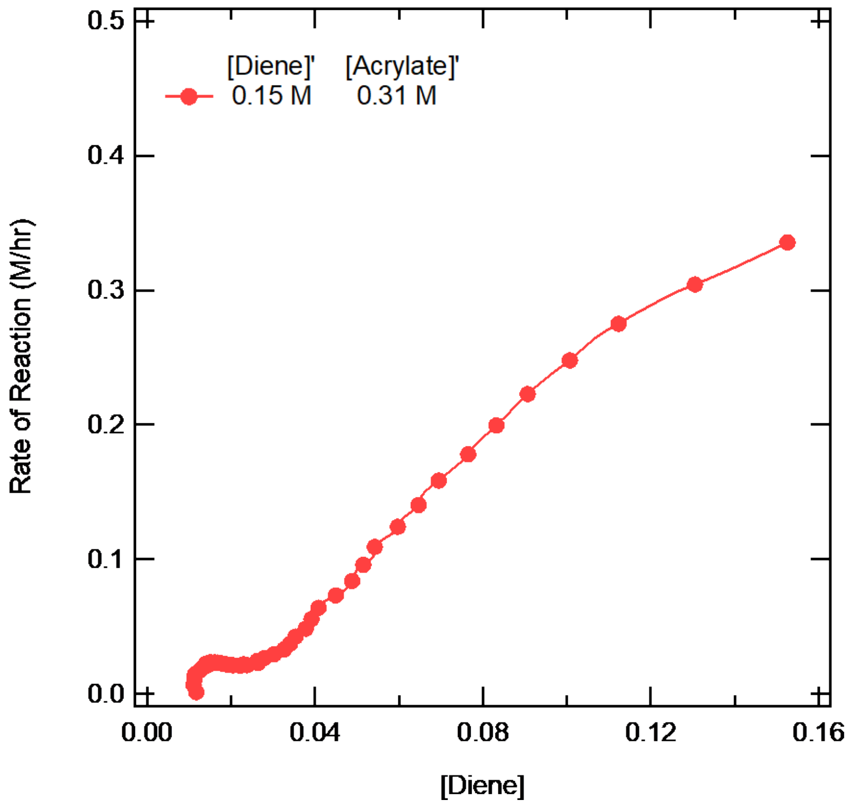


Figure SS31: The rate of diene consumption graphed against the diene concentration. Where rate of diene consumption is on the y-axis and diene concentration is on the x-axis. The rate was calculated from the polynomial fit of the diene concentration vs time graph as seen in Figure 29. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

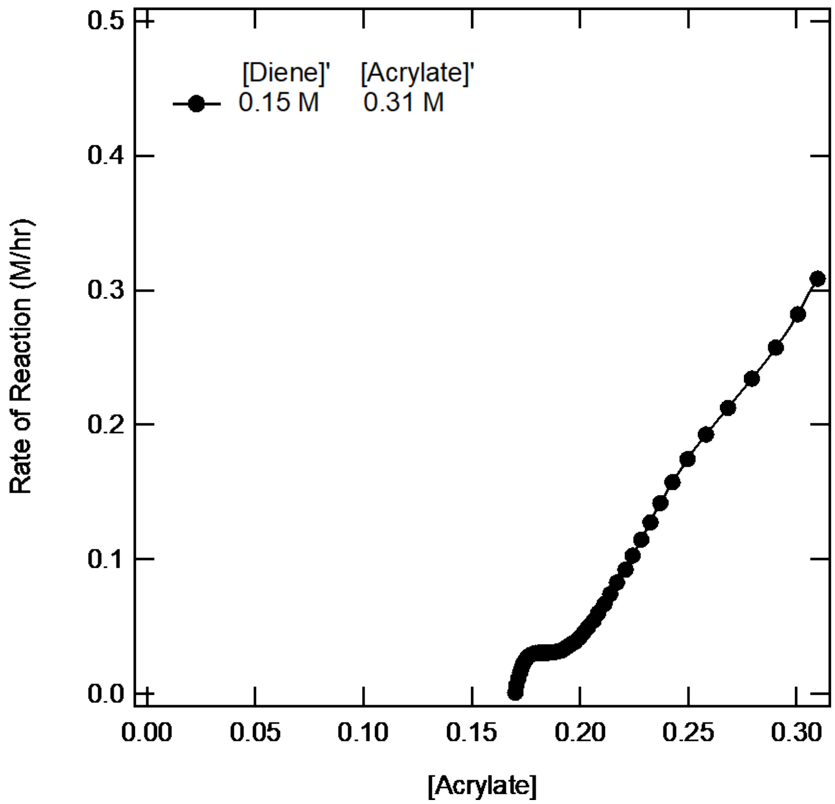


Figure SS32: The rate of acrylate consumption graphed against the acrylate concentration. Where rate of acrylate consumption is on the y-axis and acrylate concentration is on the x-axis. The rate was calculated from the polynomial fit of the acrylate concentration vs time graph as seen in Figure 30. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

Average for the 0.15 M Diene 0.31 M Acrylate

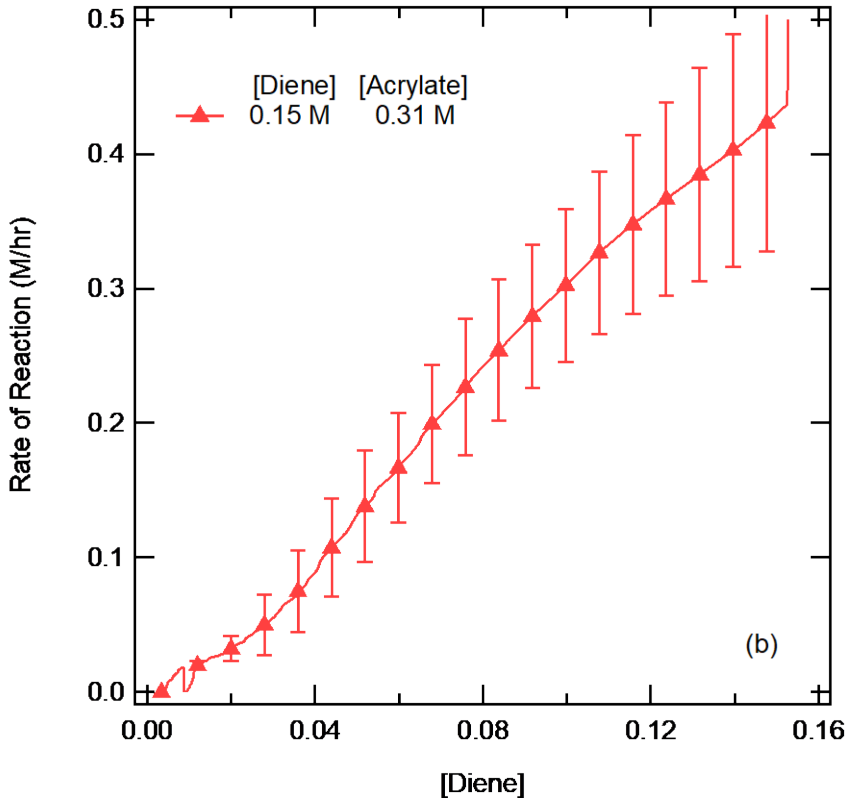


Figure SS33: The average rate of diene consumption graphed against the diene concentration. Where rate of diene consumption is on the y-axis and diene concentration is on the x-axis. The average rate was found by averaging the values found in Figure 27 and 31. The standard deviation was calculated accordingly. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

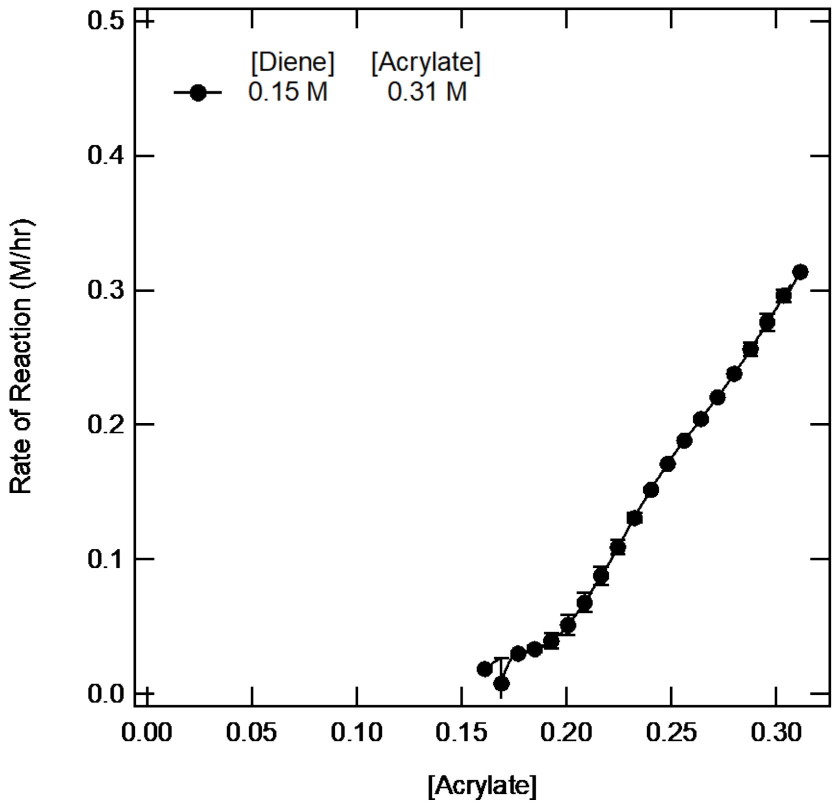


Figure SS34: The average rate of acrylate consumption graphed against the acrylate concentration. Where rate of acrylate consumption is on the y-axis and acrylate concentration is on the x-axis. The average rate was found by averaging the values found in Figure 28 and 32. The standard deviation was calculated accordingly. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

Same Excess

0.10 M Diene 0.26 M Acrylate

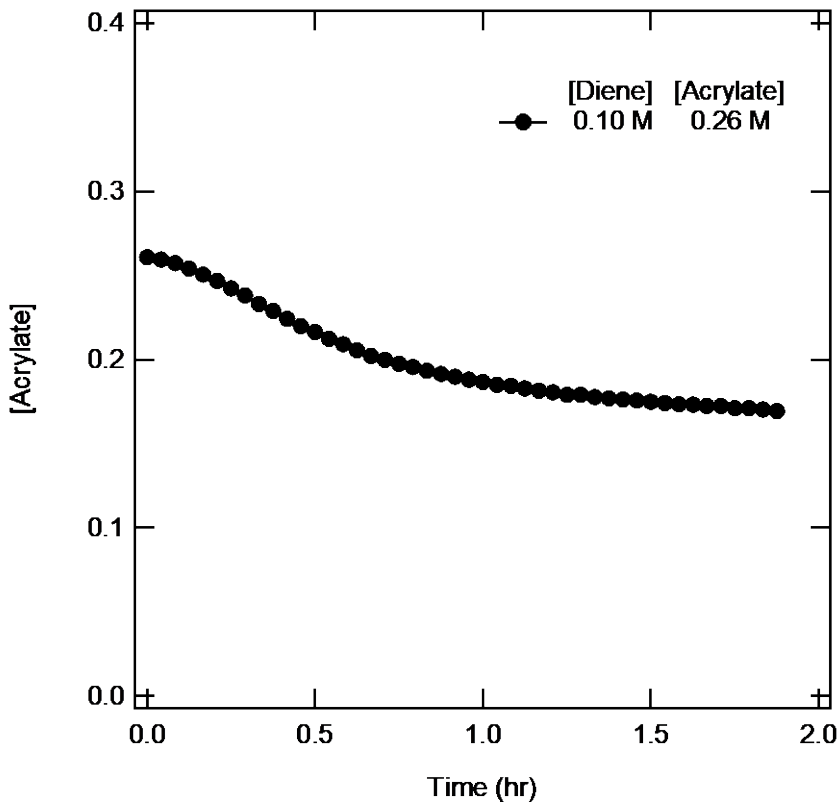


Figure SS35: The acrylate concentration vs time graph for 0.10 M diene and 0.26 M acrylate. The y-axis is the concentration of acrylate and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 1402 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

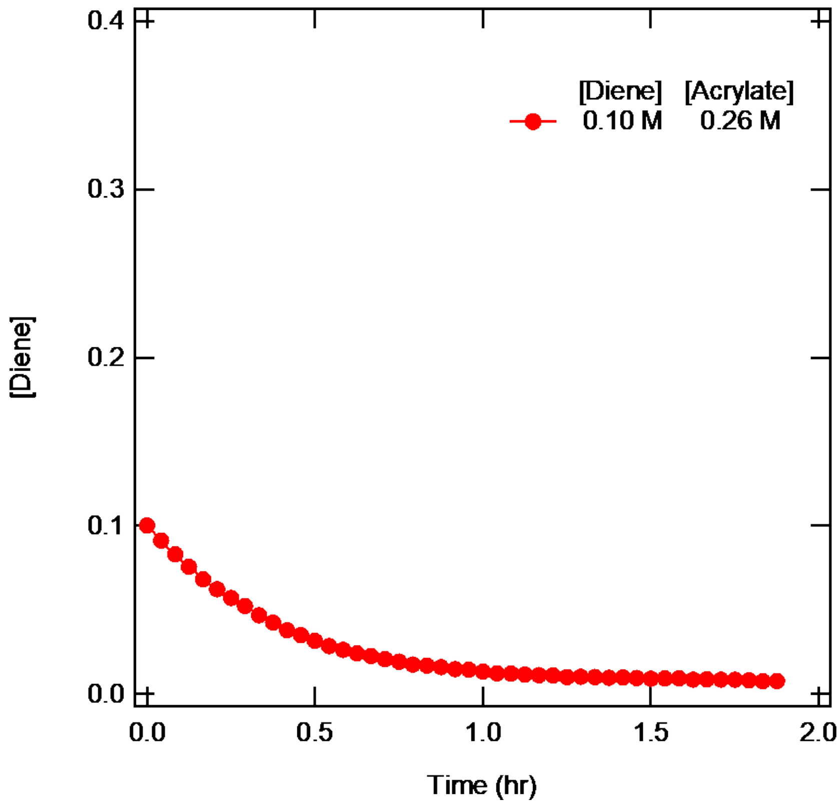


Figure SS36: The diene concentration vs time graph for 0.10 M diene and 0.26 M acrylate. The y-axis is the concentration of diene and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 896 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

0.12 M Diene 0.28 M Acrylate

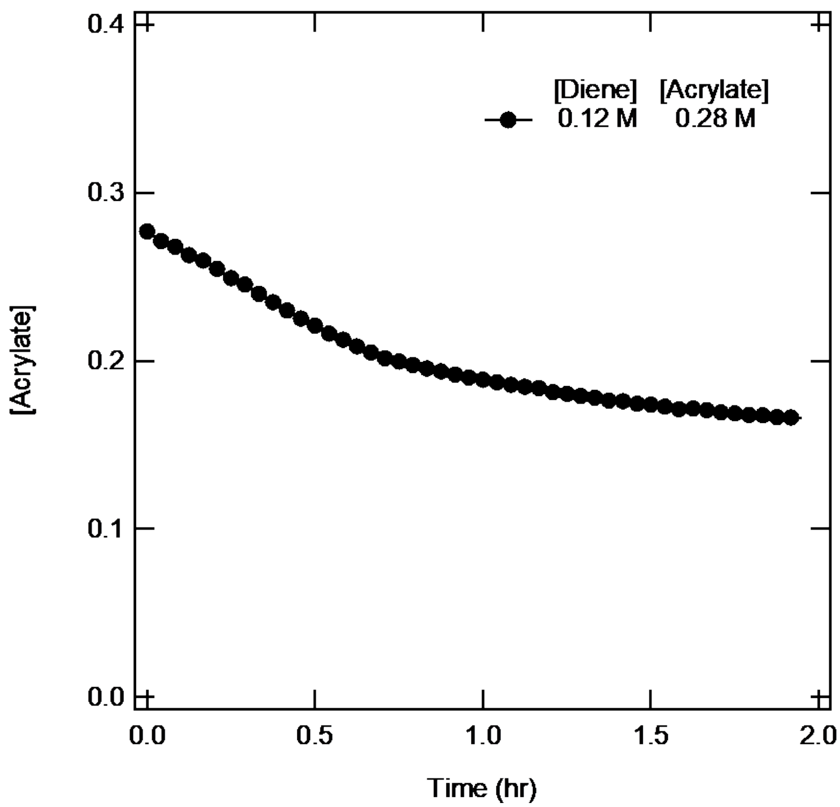


Figure SS37: The acrylate concentration vs time graph for 0.12 M diene and 0.28 M acrylate. The y-axis is the concentration of acrylate and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 1402 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

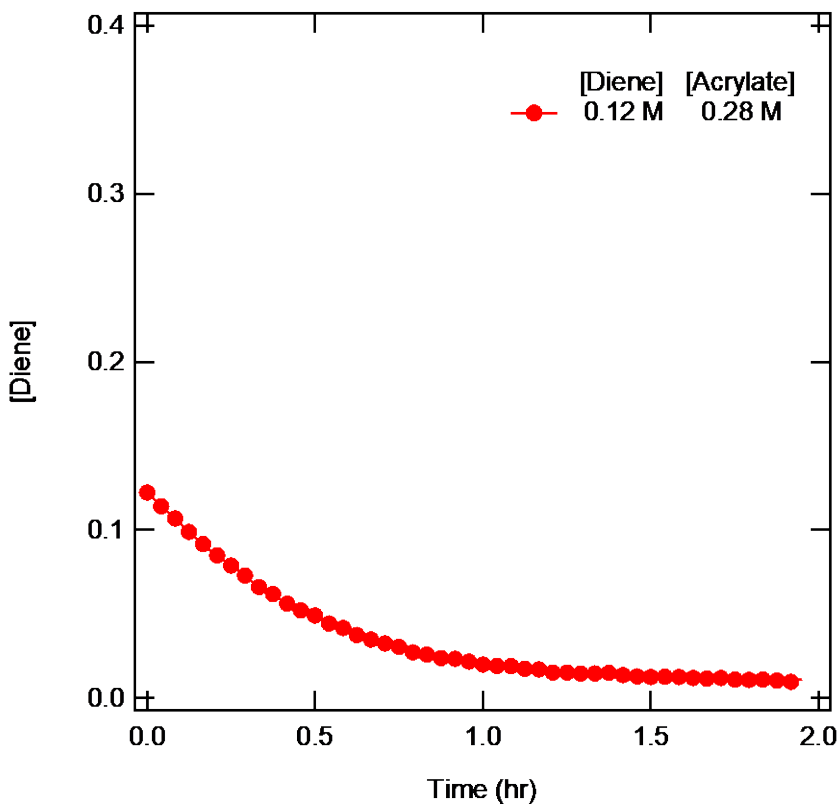


Figure SS38: The diene concentration vs time graph for 0.12 M diene and 0.28 M acrylate. The y-axis is the concentration of diene and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 896 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

0.15 M Diene 0.31 M Acrylate

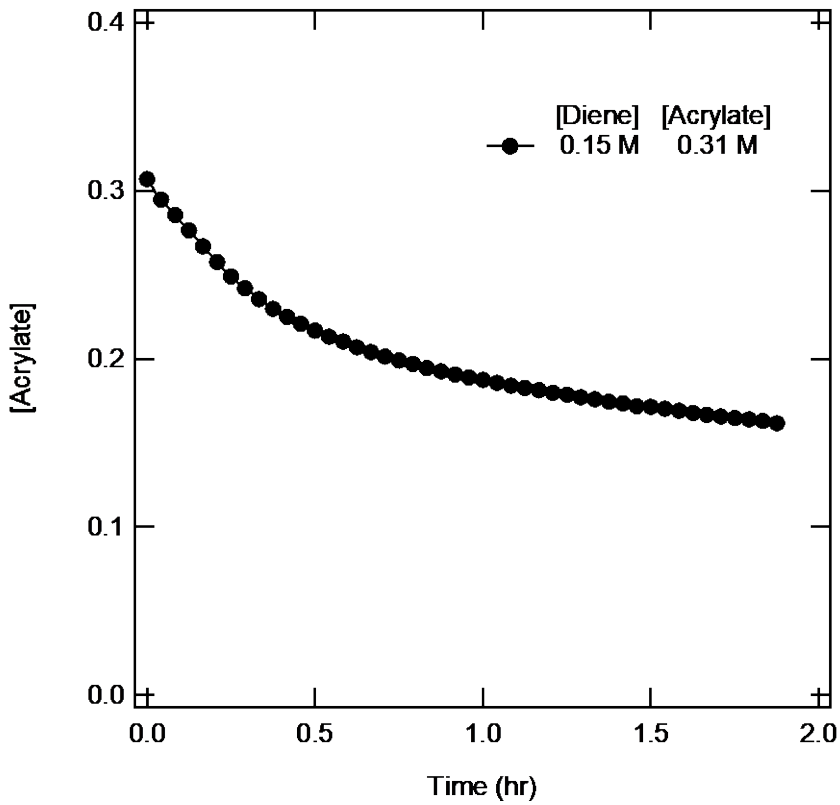


Figure SS39: The acrylate concentration vs time graph for 0.15 M diene and 0.31 M acrylate. The y-axis is the concentration of acrylate and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 1402 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

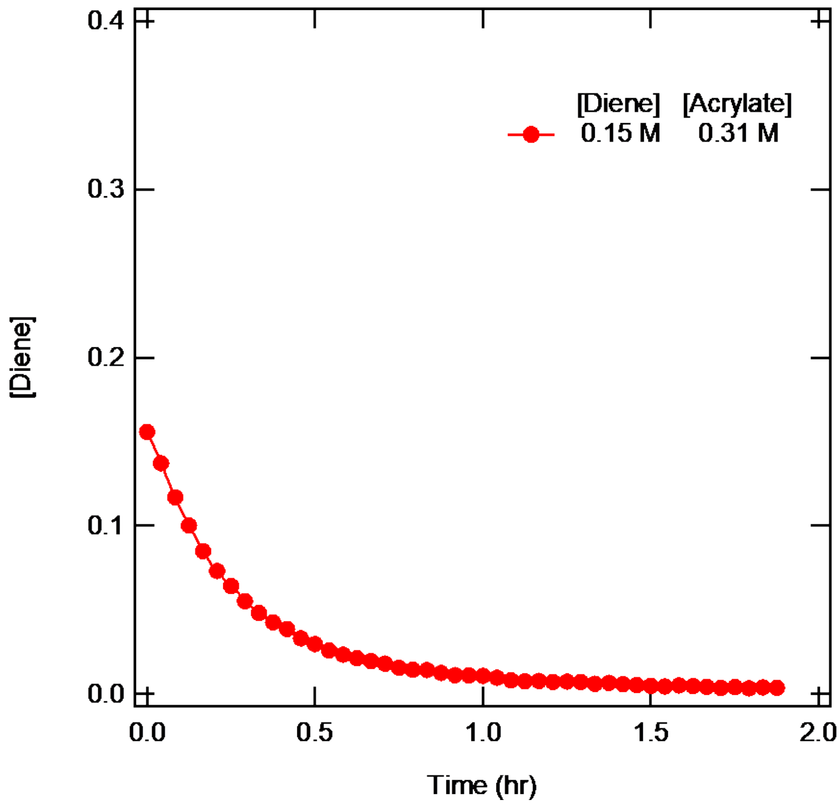


Figure SS40: The diene concentration vs time graph for 0.15 M diene and 0.31 M acrylate. The y-axis is the concentration of diene and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 896 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

0.20 M Diene 0.36 M Acrylate

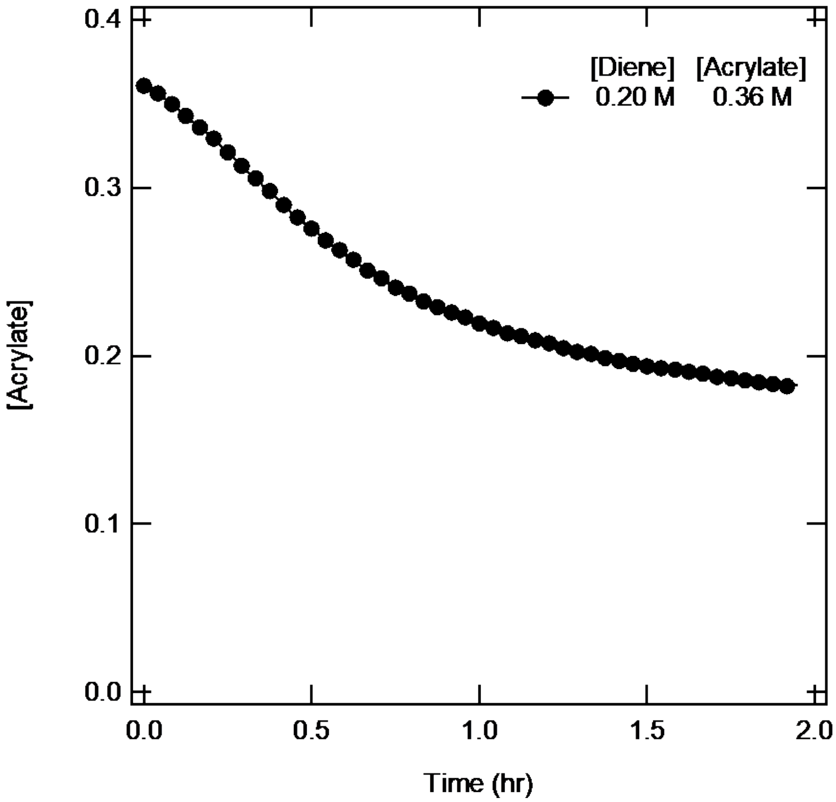


Figure SS41: The acrylate concentration vs time graph for 0.20 M diene and 0.36 M acrylate. The y-axis is the concentration of acrylate and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 1402 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

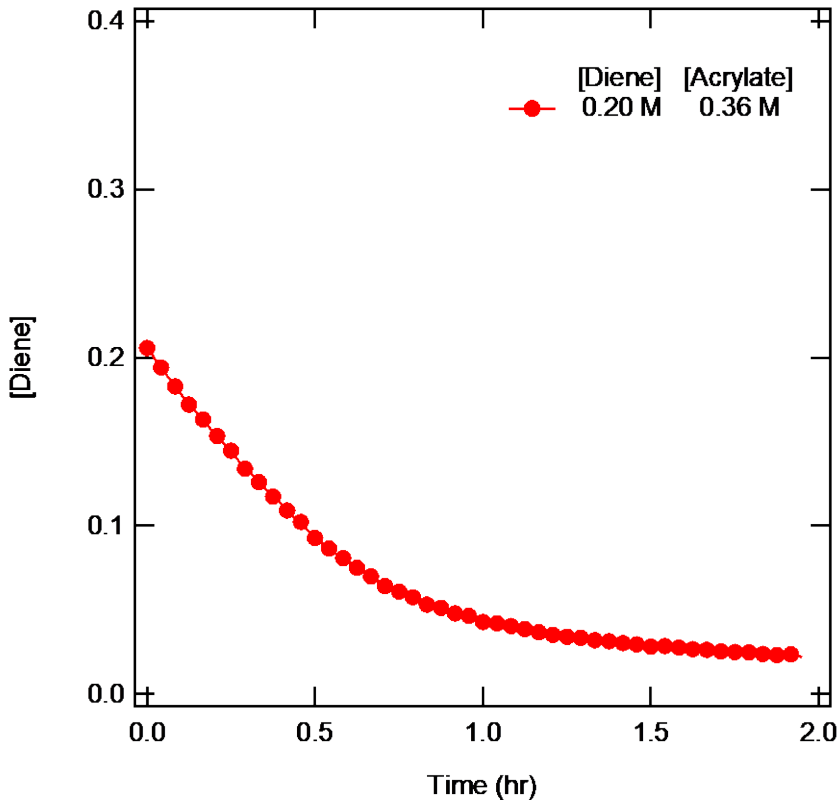


Figure SS42: The diene concentration vs time graph for 0.20 M diene and 0.36 M acrylate. The y-axis is the concentration of diene and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 896 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

Catalyst Loading Experiments.

100 mg Cat

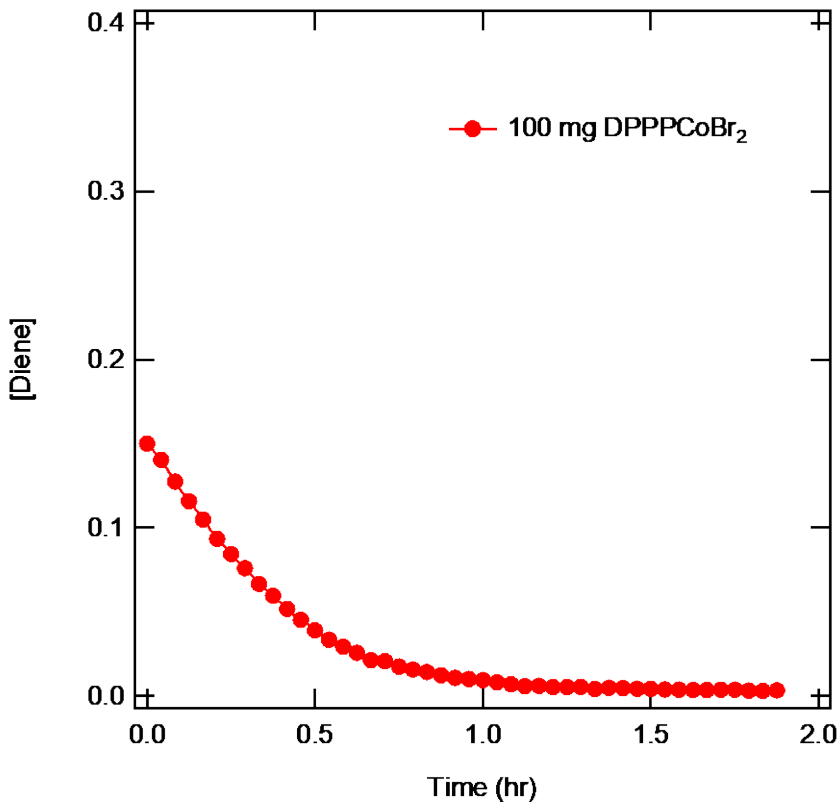


Figure SS43: The diene concentration vs time graph for 0.15 M diene and 0.31 M acrylate and 100 mg $DPPPCoBr_2$. The y-axis is the concentration of diene and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 896 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

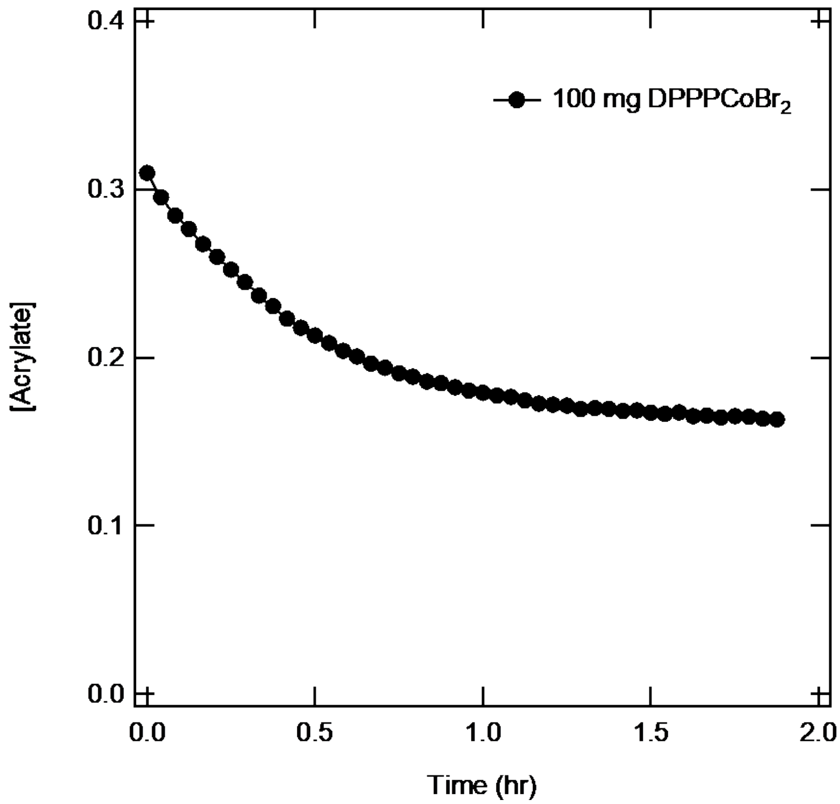


Figure SS44: The acrylate concentration vs time graph for 0.15 M diene and 0.31 M acrylate and 100 mg $DPPPCoBr_2$. The y-axis is the concentration of acrylate and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 1402 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

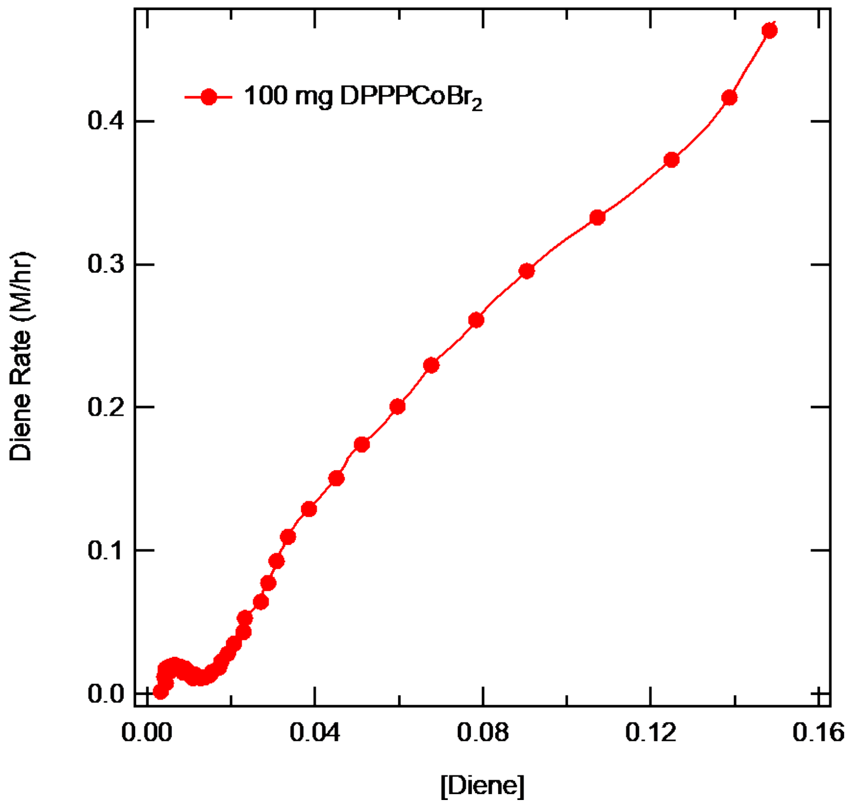


Figure SS45: The rate of diene consumption graphed against the diene concentration. Where rate of diene consumption is on the y-axis and diene concentration is on the x-axis. The rate was calculated from the polynomial fit of the diene concentration vs time graph as seen in Figure 43. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

75 mg Cat

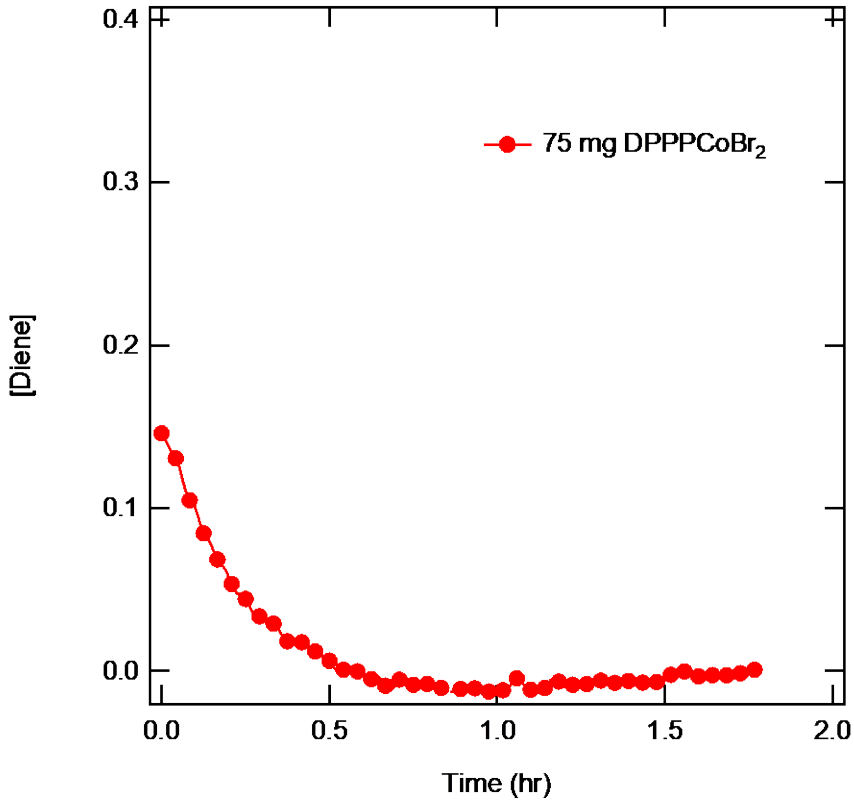


Figure SS46: The diene concentration vs time graph for 0.15 M diene and 0.31 M acrylate and 75 mg $DPPPCoBr_2$. The y-axis is the concentration of diene and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 896 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

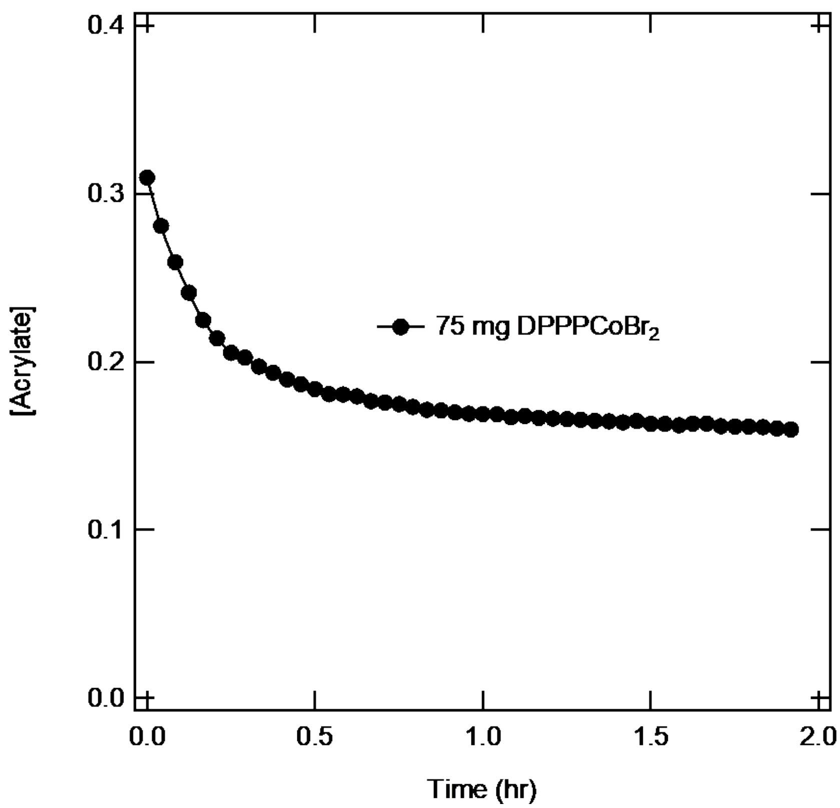


Figure SS47: The acrylate concentration vs time graph for 0.15 M diene and 0.31 M acrylate and 75 mg $DPPPCoBr_2$. The y-axis is the concentration of acrylate and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 1402 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

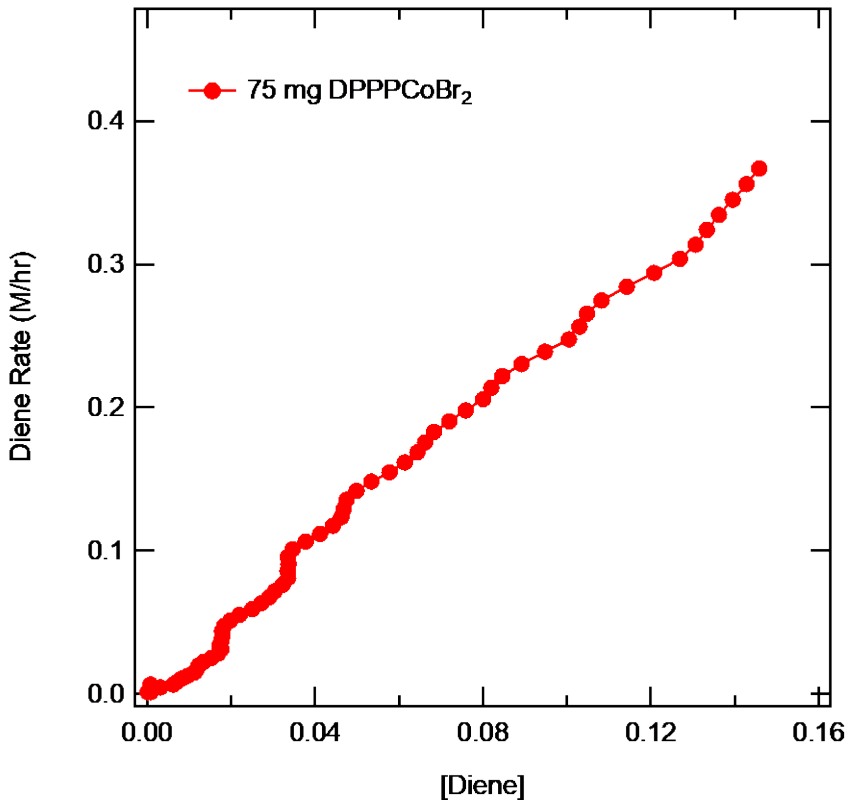


Figure SS48: The rate of diene consumption graphed against the diene concentration. Where rate of diene consumption is on the y-axis and diene concentration is on the x-axis. The rate was calculated from the polynomial fit of the diene concentration vs time graph as seen in Figure 46. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

50 mg Cat

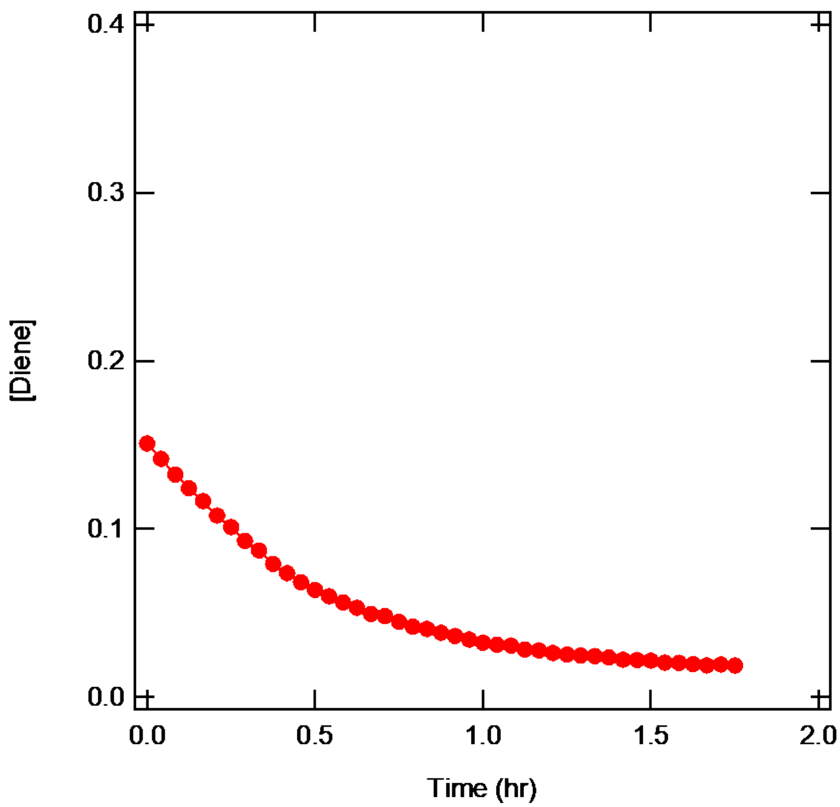


Figure SS49: The diene concentration vs time graph for 0.15 M diene and 0.31 M acrylate and 50 mg $DPPPCoBr_2$. The y-axis is the concentration of diene and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 896 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

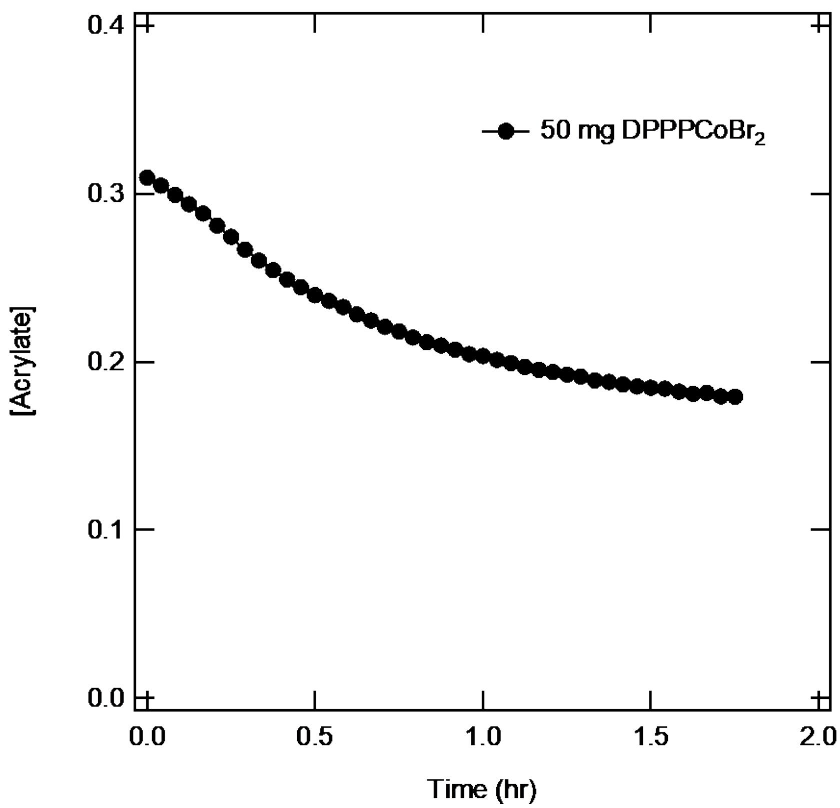


Figure SS50: The acrylate concentration vs time graph for 0.15 M diene and 0.31 M acrylate and 50 mg $DPPPCoBr_2$. The y-axis is the concentration of acrylate and the x-axis is time. This graph is obtained from the polynomial fit of the intensity vs time graph of 1402 cm^{-1}. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.

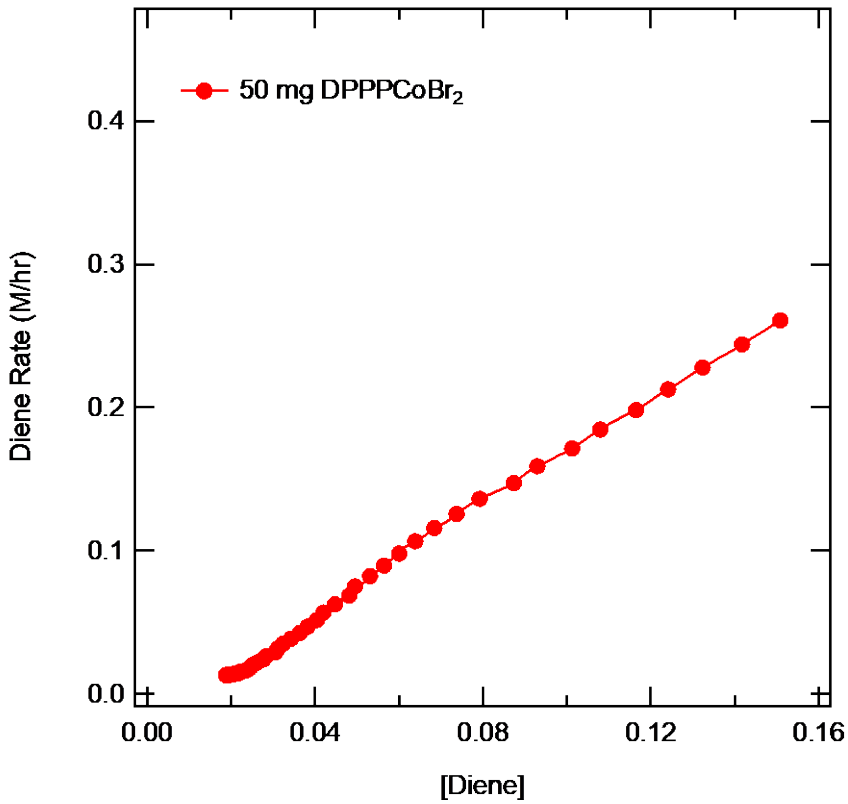


Figure SS51: The rate of diene consumption graphed against the diene concentration. Where rate of diene consumption is on the y-axis and diene concentration is on the x-axis. The rate was calculated from the polynomial fit of the diene concentration vs time graph as seen in Figure 49. The data points represent one in every five data points. The data is shown as sparse to make the information more clear.