

Anionic Polymerization and Transport of Diethyl Methylidene

Malonate on Polyolefin Copolymer Surfaces

Kelsi M. S. Rehmann, John Klier, and Jessica D. Schiffman*

Department of Chemical Engineering, University of Massachusetts Amherst, Amherst,
Massachusetts 01003-9303

*Corresponding author: Jessica D. Schiffman; Email: schiffman@umass.edu

Semi-quantitative analysis of ATR-FTIR by peak fitting and ratios of peak areas: The initial FTIR-ATR peak positions and widths of the poly(ethylene-co-acrylic acid) (control) and poly(diethyl methylenedimethyl malonate) were first fit to a Lorentzian distribution.¹⁻³ The carbonyl peak of pDEMM was fit with two Lorentzian peaks, while the carbonyl peak of pEAA was fit with one peak. The two hydrocarbon peaks for pEAA or LDPE in the 700-800 cm⁻¹ were analyzed and used as internal calibration.^{1,2}

To compare the relative amounts of pDEMM, the DEMM carbonyl peak was deconvoluted from the acrylic acid carbonyl peak, and the peak areas of the DEMM carbonyl at ~1719 cm⁻¹ and the polyolefin hydrocarbon (methylene) peak at ~719 cm⁻¹ were calculated (**Figure S1**). The ratio of the peak areas (DEMM:substrate) were compared to increase the accuracy of the analysis, similar to what was previously reported.⁴⁻⁶ The calibration curve in the grafted polymer experiment by Yamakawa was not linear, suggesting the absorbance and concentration relationship does not follow Beer's law. However, Yamakawa's calibration curve showed a good correlation between grafted polymer content and peak area ratios.⁶ Thus, the peak area ratios of the DEMM carbonyl peak to the pEAA/LDPE methylene peak were compared to monitor the effect of different substrates and spatial arrangements on pDEMM polymerization, using **Equation S1**, a simplified ratio of Beer's law:

$$\frac{A_D}{A_E} = k \frac{C_D}{C_E} \quad (\text{Equation S1})$$

in which A_D is the peak area of the DEMM carbonyl peak, A_E is the peak area of the pEAA/LDPE methylene peak, C_D is the concentration of pDEMM, C_E is the concentration of pEAA or LDPE (substrate), and k is a proportionality constant. From the model, we can see that a higher peak area ratio suggests a higher concentration of pDEMM relative to the substrate.

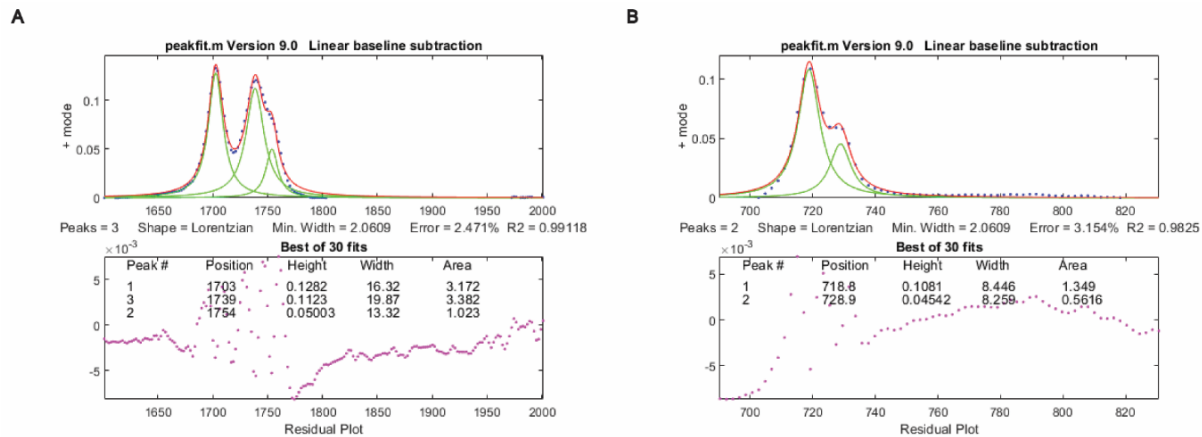


Figure S1. Representative MATLAB peak fitting using pEAA-10 grafted with pDEMM spectra. For each spectrum, two sections were fit with peaks. **(A)** The first section between 2000-1600 cm^{-1} , was fit using two peaks for pDEMM (1739 and 1754 cm^{-1}) and one peak for pEAA (1703 cm^{-1}). The peak area and height were calculated after fitting, and the error and R^2 value of the peak were noted. **(B)** The second section is for the poly(olefin) peak, which was used as an internal standard. There were two peaks in this region (shown) for the pEAA or LDPE. When an excess of pDEMM was present, other peaks occurred in this region; for the polymerized samples in which this occurred, the pDEMM peaks were modeled to deconvolute them from the poly(olefin) peaks.

Method: Testing the Potential Adsorption of pDEMM: A pDEMM (0.13 mg/mL) solution in dichloromethane (DCM) was prepared, to which a pEAA-10-Na substrate was added and allowed mix at room temperature for 24 hr.

Results: A small amount of pDEMM was observed on the surface of the pEAA-10-Na substrates after adsorption (green spectra in **Figures S2-3**). **Figures S2-4** shows that the relative amount of carboxylic acid carbonyl at $\sim 1704\text{ cm}^{-1}$ (pEAA-10) was smaller for the “grafted” sample than the adsorption sample. Additionally, the peak height for the “grafted” sample” was between the peak heights associated with the partially neutralized and very neutralized samples, suggesting that the difference in peak height does not fully correlate with the extent of neutralization. This suggests that some of the carboxylic acid was consumed in the grafting reaction. Additionally, when a similar overlay was conducted with the pDEMM surface initiated on the pEAA-10 substrate and compared to the pEAA-10 substrate, the carbonyl peak height also decreased for the pDEMM surface initiated sample.

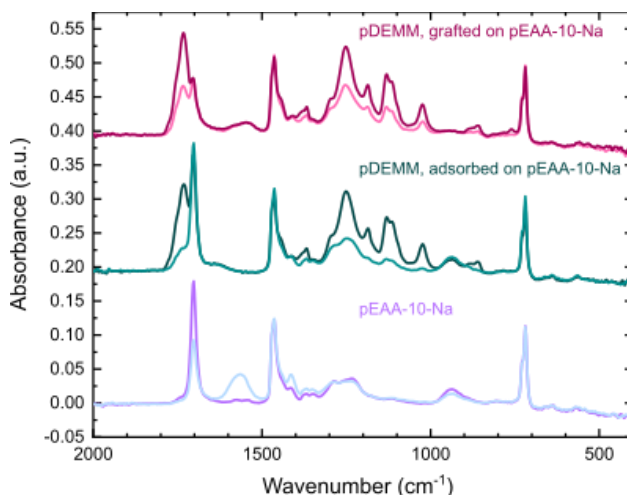


Figure S2. Spectra comparing pDEMM on pEAA-10-Na after surface initiation procedure (pink) to pDEMM adsorbed from dichloromethane (green), and to neutralized pEAA-10-Na substrate (purple). Note that two different spectra were acquired at different sections of the same film, which are provided for each sample type.

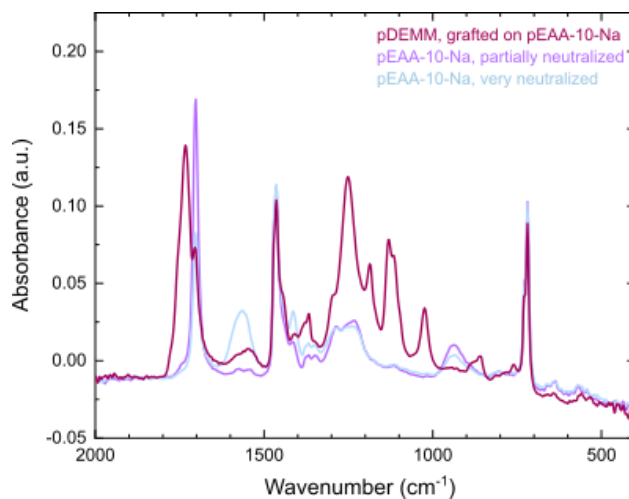


Figure S3. Overlaid spectra of pDEMM on pEAA-10-Na after surface initiation procedure (pink) and pEAA-10-Na substrate (purple).

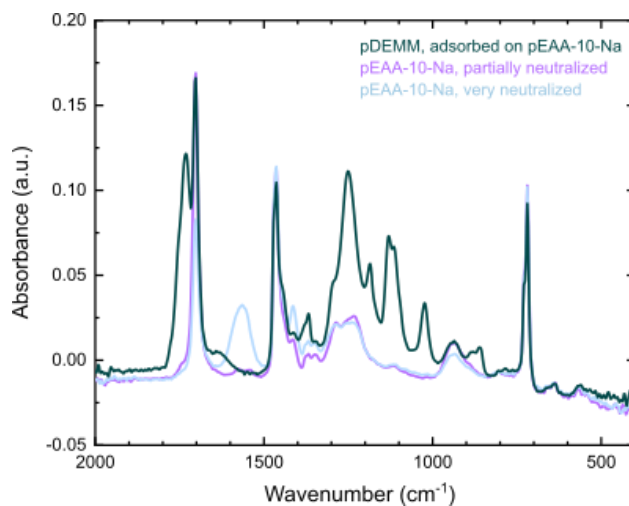


Figure S4. Overlay of pDEMM on pEAA-10-Na adsorbed from dichloromethane (green) and pEAA-10-Na substrate (purple).

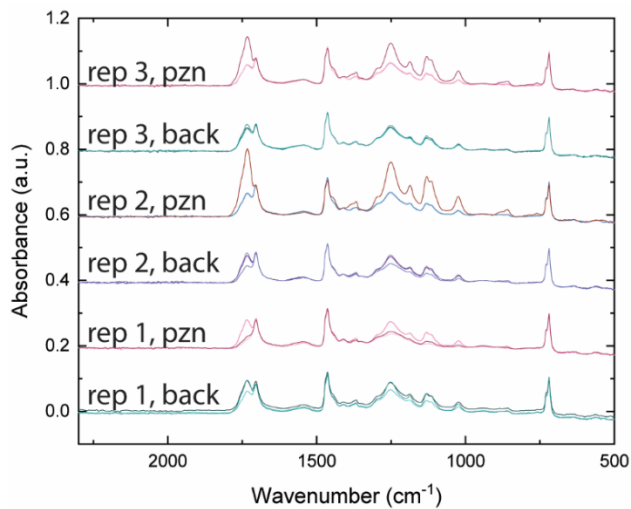


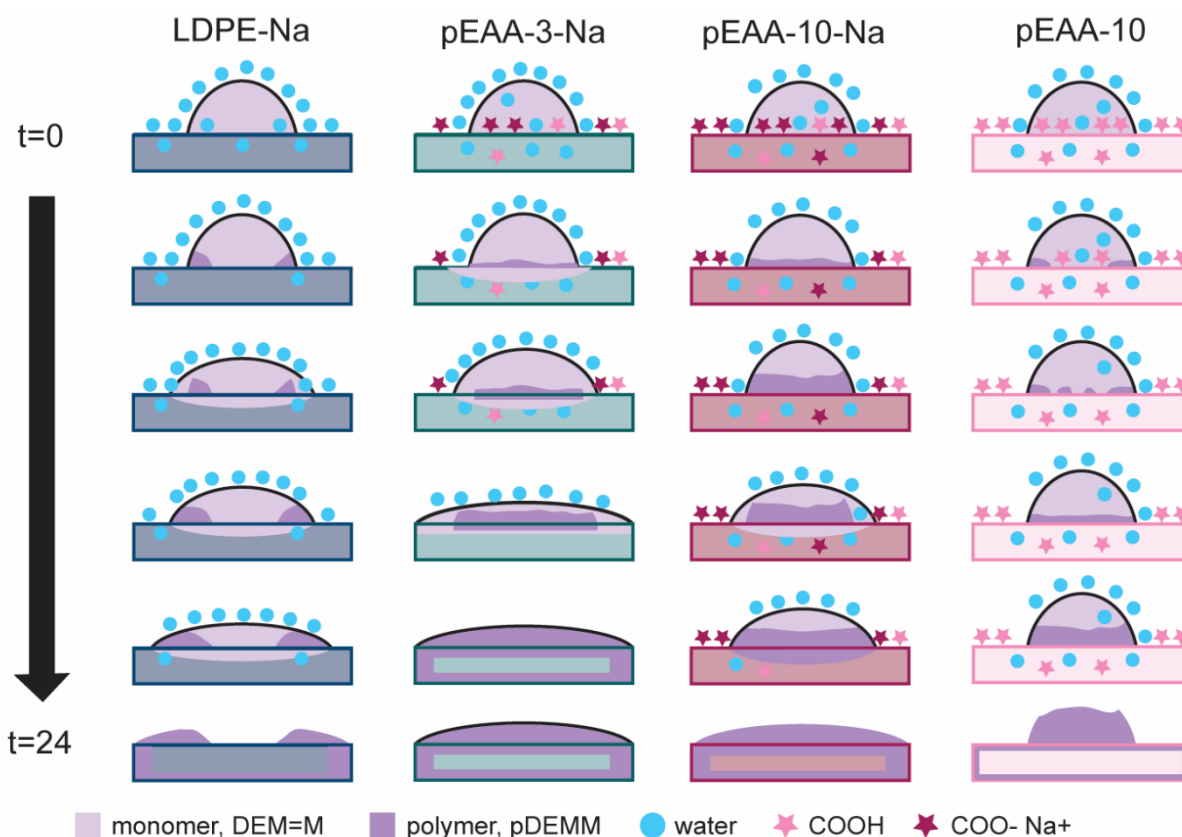
Figure S5. Three replicate (rep) spectra, acquired from various locations on the pEAA-10-Na substrates after pDEMM polymerization and chloroform wash, are overlaid. Spectra from the polymerization side of the film (pzn) and from the back side of the film (back) are provided.

Table S1. Heat map values for polymerization data, associated with **Figure 4**. Underlined values represent data with difficult to deconvolute poly(olefin) internal standard peaks whereas “—” denotes when the internal standard peaks were absent or could not be deconvoluted. Quadrant 1 starts in the “top left” part of the image and quadrants are labeled clockwise.

Sample		Bottom			Top		
		Quadrant 1	Quadrant 3	Center	Quadrant 1	Quadrant 3	Center
LDPE-Na	Avg	10.1	7.9	1.4	—	—	0.4
	StDev	2.5	4.9	1.2	—	—	0.4
pEAA-3-Na	Avg	6.8	8.8	5.2	<u>149.9</u>	<u>28.8</u>	—
	StDev	2.9	1.5	1.0	92.9	8.9	—
pEA-10-Na	Avg	19.6	13.8	8.7	36.2	31.9	—
	StDev	4.8	1.7	1.4	17.3	2.1	—
pEAA-10	Avg	1.4	1.2	0.9	10.3	10.0	14.8
	StDev	1.0	1.2	0.9	5.6	5.2	8.8

Table S2. Heat map values for grafting data, associated with **Figure 5**. Quadrant 1 starts in the “top left” part of the image and quadrants are labeled clockwise.

Sample		Bottom			Top		
		Quadrant 1	Quadrant 3	Center	Quadrant 1	Quadrant 3	Center
LDPE-Na	Avg	0.1	0.1	0.1	0.1	0.1	0.1
	StDev	0.1	0.1	0.1	0.1	0.1	0.1
pEAA-3-Na	Avg	0.2	0.2	0.2	0.5	0.5	0.9
	StDev	0.1	0.1	0.1	0.3	0.2	0.7
pEA-10-Na	Avg	1.5	1.0	0.8	1.4	1.1	3.5
	StDev	0.2	0.8	0.6	0.5	0.1	1.5
pEAA-10	Avg	0.1	0.1	0.1	1.3	1.7	5.8
	StDev	0.1	0.1	0.2	1.2	1.4	5.0



Schematic S1. Schematic displaying our hypothesis for reactive transport mechanism. The substrate is labeled at the top of the column; moving down the column represents increasing time (hr).

References

- 1 B. Smith, *Infrared spectral interpretation: A systematic approach*, CRC Press, Boca Raton, FL, 1998.
- 2 B. C. Smith, *Fundamentals of Fourier transform infrared spectroscopy*, CRC Press, Inc., Boca Raton, FL, 1st edn., 1996.
- 3 B. C. Smith, *Spectroscopy*, 2016, **31**, 14–21.
- 4 M. K. Bellamy, *J Chem Educ*, 2010, **87**, 1399–1401.
- 5 F. M. Mirabella, *Journal of Polymer Science: Polymer Physics Edition*, 1982, **20**, 2309–2315.
- 6 S. Yamakawa, *J Appl Polym Sci*, 1976, **20**, 3057–3072.