

Infrared process monitoring of conjugated linoleic acid/styrene/butyl acrylate bulk and emulsion terpolymerization

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ABSTRACT: Free radical bulk and emulsion co- and terpolymerizations of conjugated linoleic acid (CLA) with styrene (Sty) and butyl acrylate (BA) were performed at 80 °C. The polymerizations were monitored using an attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopic probe. Bulk polymerizations were monitored off-line while emulsion polymerizations were monitored in-line. Absorbance peaks related to the monomers and polymer were tracked to provide conversion and polymer composition data using a multivariate calibration method. Off-line measurements using gravimetry and ¹H-NMR spectroscopy were compared to the ATR-FTIR data and no significant differences were detected between the measurement methods. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43574.

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INTRODUCTION

Significant effort is currently being made to replace petroleum-based monomers with more sustainable polymer building blocks. Plant oils offer built-in degradability if cross-linking is not excessive, lower product toxicity,¹ and lower gross energy requirement¹ therefore satisfying several green chemistry principles.² Plant oils can be less energy intensive to produce than alcohols or sugars because they do not require solvent extraction or intensive heat input. Even if pressing can produce lower yields, the biomass residue called seedcake and comprised mainly of proteins, can be used elsewhere such as in animal feed.³ Plant oils are made of triglycerides and they consist of a glycerol center with three fatty acid chains. The polymerization of smaller fatty acid chains such as linoleic acid should reduce the steric hindrance associated with the polymerization of the larger triglycerides.⁴ Since it appears that conjugated oils copolymerize and non-conjugated oils invoke degradative chain transfer,⁵ conjugated linoleic acid (CLA) is preferred for free radical polymerizations. Several production methods exist for CLA^{6–10} but it can also be produced simply and inexpensively from soybean oil photo-isomerization.¹⁰ In previous work, we reported on the copolymerization and terpolymerization of CLA with styrene (Sty) and butyl acrylate (BA),^{11–13} where oleic acid was shown to have a significant impact on the reaction kinetics for bulk and emulsion reactions.

An important principle of green chemistry involves the real-time monitoring of processes.² The inline monitoring of polymerizations using an attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy would satisfy this green chemistry principle and has already been applied to monitoring conversion and polymer composition in our laboratory.^{14–16} In this technique, a sample is placed in contact with an internal reflection element (IRE) with a high refractive index and low infrared absorption in the region of interest. When the infrared beam enters the IRE at an angle just below the critical angle for total internal reflection, an evanescent wave is set up and is designed to penetrate 1–10 μm into the sample.¹⁷ Since the infrared frequencies are similar to the vibrational movements of chemical bonds, the sample will only absorb infrared frequencies matching its own vibrational movements. The remaining infrared beam (or reflection spectra) can be detected to analyze which frequencies were absorbed. This remaining infrared beam intensity will not decrease significantly because the intensity of the evanescent wave decays exponentially with the distance from the IRE, thus allowing thick or strongly absorbing samples (e.g., water) to be analyzed.¹⁷ The frequencies absorbed in the reflection spectra can be associated with functional groups in polymer chains.¹⁸ A quantitative analysis is made possible by applying Beer's law, which stipulates that the absorbance intensity at a certain frequency is proportional to the concentration of the associated component.¹⁸ For the measurement of the

Table I. Feed Composition for Bulk and Emulsion Experiments

Bulk reactions	f_{CLA} (mole fraction)	f_{Sty} (mole fraction)	f_{BA} (mole fraction)
1	0.078	-	0.922
2	0.160	-	0.840
3	0.246	-	0.754
4	0.337	-	0.663
5	0.431	-	0.569
6	0.534	-	0.466
7	0.640	-	0.360
8	0.753	-	0.247
9	0.872	-	0.128
10	0.078	0.922	-
11	0.160	0.840	-
12	0.247	0.753	-
13	0.338	0.662	-
14	0.432	0.568	-
15	0.533	0.467	-
16	0.640	0.360	-
17	0.754	0.246	-
18	0.872	0.128	-
19	0.078	-	0.922
20	0.203	-	0.797
21	0.338	-	0.662
22	0.075	0.925	-
23	0.197	0.803	-
24	0.338	0.662	-
25	0.076	0.103	0.821
26	0.156	0.105	0.740
27	0.240	0.108	0.652
28	0.329	0.111	0.560
29	0.424	0.116	0.461
30	0.524	0.119	0.356
31	0.746	0.127	0.127
32	0.075	0.821	0.103
Emulsion reactions	f_{CLA} (mole fraction)	f_{Sty} (mole fraction)	f_{BA} (mole fraction)
1-25	0.077	0.103	0.820
26-31	0.119	0.104	0.777
32-40	0.161	0.105	0.734

reflection spectra, an interferometer is used and a Fourier transform is applied to enhance the spectral resolution. Infrared spectroscopy includes three distinct spectral regions; namely near-infrared (NIR), mid-infrared (MIR), and far-infrared (FIR). The MIR spectral region encompasses the frequencies corresponding to the fundamental vibrations of virtually all functional groups of organic molecules.¹⁸ In this article, we describe the application of ATR-FTIR spectroscopy to the monitoring of bulk and emulsion co- and terpolymerization of CLA, Sty, and BA.

EXPERIMENTAL

Materials

Conjugated linoleic acid (CLA), (Penta, 74 mol % CLA, 13 mol % oleic acid, 13 mol % saturated fatty acid, inhibitor-free) was chosen for economic reasons and was used without further purification. One should note that the saturated fatty acid portion of the CLA is non-reactive whereas the oleic acid portion plays the role of an impurity.¹¹⁻¹³ For bulk reactions, the reagents styrene (Sty, Sigma-Aldrich, 99%) and butyl acrylate (BA, Sigma-Aldrich, 99%) were purified to remove the inhibitor, hydroquinone. The initiator, benzoyl peroxide (BPO, Sigma-Aldrich, 100%), and all solvents (e.g., methanol (Fisher, 99.9%) and chloroform-d [Cambridge Isotope Laboratories, 99.8%]), were used as received.

For the emulsion polymerizations, the reagents Sty and BA were used as received. A water-soluble initiator, potassium persulfate (KPS, Fisher, 100%), was used along with the emulsifier, sodium dodecyl sulfate (SDS, EM Science, 100%), and distilled deionized (DDI) water as the suspending medium. In some instances, additives such as sodium bicarbonate (NaHCO₃, Fisher, 100%), n-dodecyl mercaptan (chain transfer agent (CTA), Sigma Aldrich, 98+%), acrylic acid (AA, Acros, 99.5%), and divinylbenzene (DVB, Sigma Aldrich, 80%) were added to modify the latex properties.

Polymerizations

Bulk polymerizations were performed at 80 °C in glass ampoules with 1 cm outside diameter and 17 cm in length (~2-3 g of monomer in each ampoule). The concentration of initiator, BPO, was 2 phm (parts per hundred parts monomer on a mass basis) for all bulk experiments. To remove oxygen, three freeze-pump-thaw cycles were performed on each ampoule before flame-sealing them. The sealed ampoules were then submerged in a preheated oil bath for a known amount of time before being removed and quenched in an ice bath for 10 min. All samples were analyzed for conversion and polymer composition.

Emulsion polymerizations were performed at 80 °C in a 1.2 L, jacketed glass reactor with a Labmax setup and stirred at 200 rpm. The reactor was equipped with a nitrogen pressurizing line, a sampling line, a vent with reflux condenser, and a port for an infrared (IR) probe. CLA, Sty, BA, CTA, AA, DVB were mixed for 15 min while DDI water, SDS, and NaHCO₃ were also mixed for 15 min in a separate beaker. The two solutions were then combined and mixed for 45 min before being poured into the reactor. The oxygen was purged from the emulsion with nitrogen for 45 min while the reaction temperature was raised. After the reaction mixture reached 80 °C, a deoxygenated initiator solution was pumped into the reactor and this marked the beginning of the polymerization. Samples were taken regularly through the sampling line for offline analyses by gravimetry and ¹H-NMR spectroscopy.

Characterization

For the bulk polymerizations, mass conversion based on the total polymer in the reaction mixture was measured using gravimetry. The reaction mixture (~3 g) was first dissolved in acetone (~10 mL) and then ~125 mL of methanol was used to

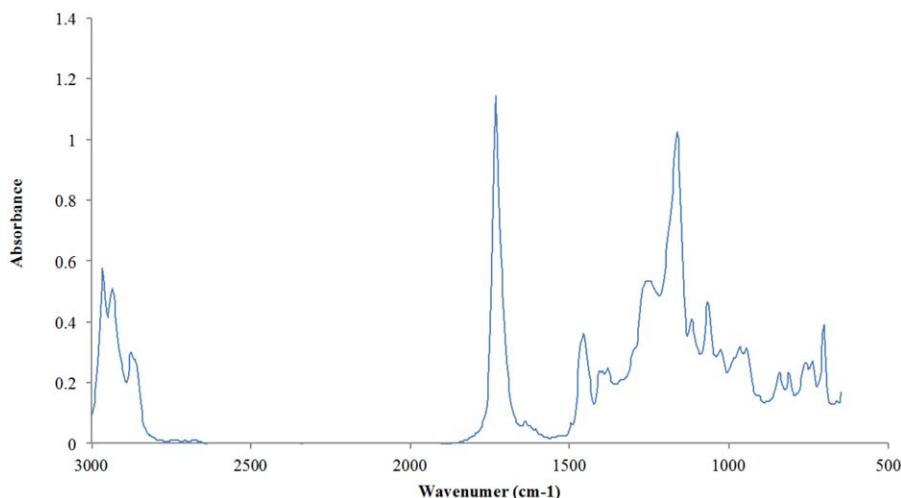


Figure 1. Example ATR-FTIR spectrum for bulk CLA/Sty/BA (26/13/61 mol/mol/mol) terpolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

precipitate the polymer. The soluble portion of the sample mixture was decanted and the polymer/methanol samples were left to dry in a fumehood for ~ 7 days, then under vacuum for ~ 7 days until a constant weight was reached. The composition from the polymer/methanol samples was used to perform a mass balance and calculate monomer conversion and polymer compositions.

For the emulsion polymerizations, samples of ~ 3 – 10 g were taken for off-line testing by gravimetry and $^1\text{H-NMR}$ spectroscopy. The samples were dried for ~ 7 days in the fumehood and ~ 7 days in a vacuum oven at room temperature, until a constant weight was achieved. The mass of CLA monomer, oleic acid, and saturated fatty acid left in the dry sample were subtracted from the measured dry sample mass to calculate the dry polymer conversion.^{11–13}

$^1\text{H-NMR}$ spectroscopy was used to determine the cumulative copolymer composition. Analyses were carried out at room temperature in deuterated chloroform ($\sim 2\%$ w/v) with a Bruker

AVANCE III 400 Fourier transform $^1\text{H-NMR}$ spectrometer. The acquisition time was 4.6 sec and 16 scans were performed per sample. A detailed presentation of peak assignments and calculation procedure for copolymer and terpolymer composition was reported previously.^{11–13}

The bulk polymerizations were monitored offline with a ReactIR 45m (Mettler Toledo) reaction analysis system for collecting MIR spectra (4000 – 650 cm^{-1}) of the polymer/monomer mixture. The ReactIR 45m was equipped with fiber optic technology for signal transmission from a stainless steel probe. The IRE element of the probe is a diamond composite (DiComp) material. The spectra were collected at a resolution of 8 cm^{-1} with a variable number of scans per sample, which were on average, 128 scans were per sample. For the emulsion polymerizations, spectra were collected in-line, every minute until the end of the reaction. An IR air background spectrum was collected from the empty reactor prior to adding the emulsion formulation.

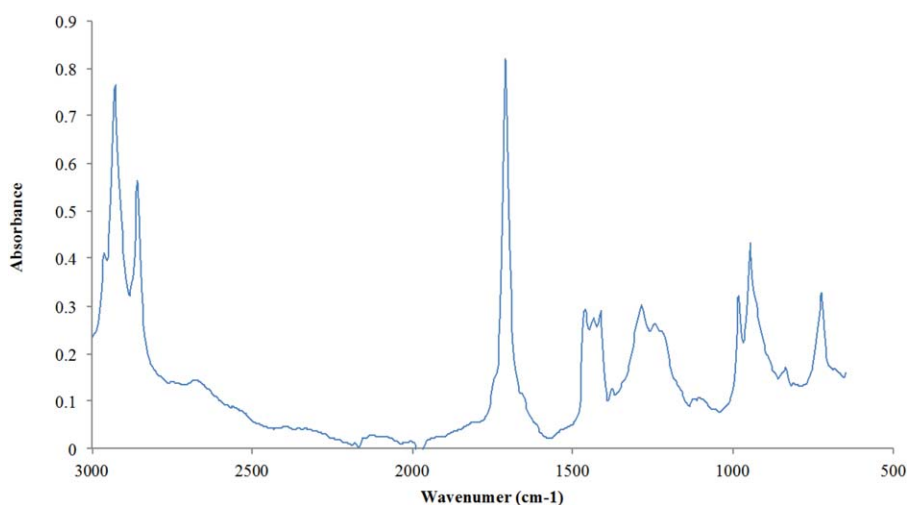


Figure 2. ATR-FTIR spectrum of CLA monomer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

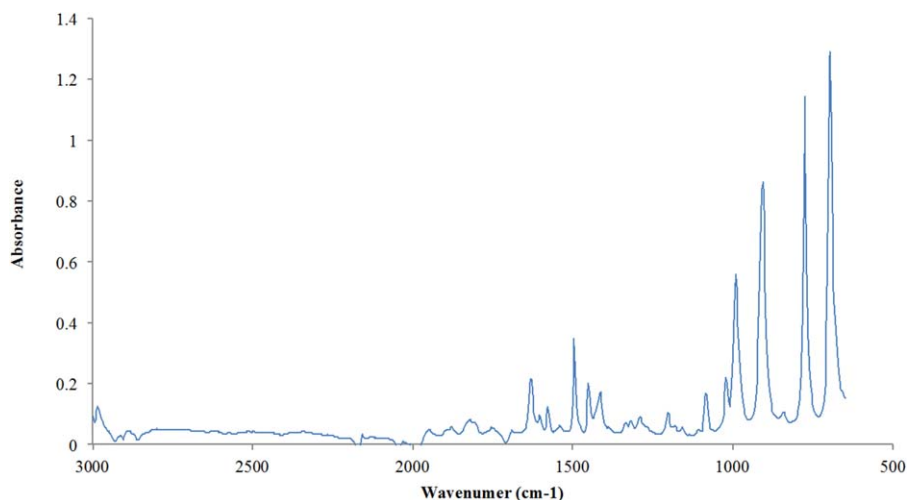


Figure 3. ATR-FTIR spectrum of Sty monomer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

In an attempt to validate the ATR-FTIR monitoring method for the bulk polymerizations, a series of CLA/Sty, CLA/BA, and CLA/Sty/BA bulk experiments at several different compositions were performed at 80 °C. At the end of the reaction, an IR spectrum of the mixture was taken and the resulting polymer was characterized for polymer composition and conversion using $^1\text{H-NMR}$ spectroscopy and gravimetry. The ATR-FTIR monitoring method was then extended to a series of CLA/Sty/BA emulsion polymerizations where the reaction was monitored in-line. Occasional off-line sample characterization was performed using $^1\text{H-NMR}$ spectroscopy and gravimetry to validate the results. Both the bulk and emulsion polymerization off-line conversion and polymer composition results were reported previously.^{11–13} The in-line ATR-FTIR approach provides interesting insight into the initial fast production of CLA-rich oligomers compared to the offline measurements where infrequent measurements did not provide a full composition profile in the early reaction stages. Comparison of past work with the bulk terpolymer¹²

and that with the emulsion terpolymer¹³ reveals no significant differences between the respective composition profiles. This leads to the conclusion that a mass transfer limitation on CLA is unlikely; another interesting insight provided by the in-line ATR-FTIR method. As noted earlier, our industrial grade CLA contains saturated fatty acid, oleic acid, and CLA. The saturated fatty acid component does not contain the double bonds necessary for free radical polymerization and does not participate in the polymerization, thus any detectable change in its IR functional group peaks would not be expected. The oleic acid component does not add to the polymer chains although it participates as an electron trap. In addition, it has been shown to act as an emulsifier,¹³ and it too would not present any detectable changes in its IR functional group peaks.

Table I shows the feed compositions for the bulk and emulsion polymerizations. It should be noted that 32 different bulk formulations and 40 emulsion formulations were used. For the emulsion polymerizations, some runs contained small amounts of acrylic acid, CTA, and DVB to modify latex properties.¹³ The

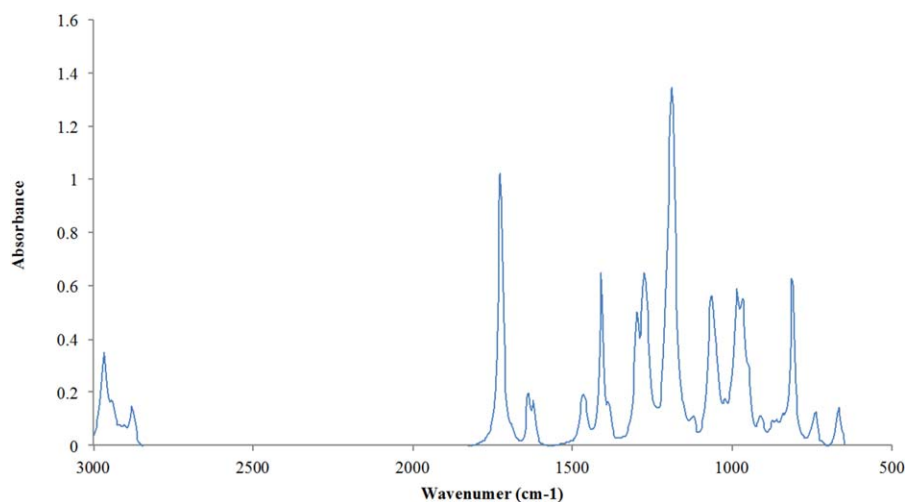


Figure 4. ATR-FTIR spectrum of BA monomer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. IR Peak Assignments for CLA,^{19,20} Sty,²¹ and BA²²

Material	Wavenumber (cm ⁻¹)	Functional group	Comment
CLA	720	-(CH ₂) _n -	aliphatic chains
	948	=C-H vibration	cis, trans dienes
	982	=C-H vibration	cis, trans dienes
	1160	C-O-C on ester group	
	1650	if non-conjugated	no peaks
	1745	-COOH groups	
	2930-2850	-CH ₂ - groups	
	2960	methyl group end	Shoulder
	3002	C-H stretching	cis, trans isomer
	3020	C-H stretching	cis, trans isomer
poly-CLA	1711	-COOH groups	
	2856	-CH ₂ - groups	
	2927	-CH ₂ - groups	
Sty	696.6	ring bending	
	773.7	ring C-H wag	
	906.9	-CH ₂ wag	
	991.8	-CH wag	
	1412	=CH ₂ deformation	
	1449	ring semi-circle stretching	
	1495	ring semi-circle stretching	
	1630	C=C stretching	
	3010	-CH stretching	
	poly-Sty	1066	ring semi-circle stretching
1166		-CH-CH ₂ wag	
1367		-CH-CH ₂ wag	
2856		-CH ₃ asymmetric stretching	
2927		-CH ₂ asymmetric stretching	
BA	668	C=O wagging	
	810	=CH ₂ twisting	
	1063	=CH ₂ rocking	
	1187	=C-(C=O)-O-CH ₂ stretching	aliphatic ester
	1273	=CH rocking	
	1409	C-H deformation in =CH ₂	
	1725	C=O stretching	
	2950-2850	aliphatic C-H stretching	
poly-BA	1470	C-H deformation	methyl band
	1740	C=O stretching	

primary target application for the emulsion polymerizations was as a pressure-sensitive adhesive and as such, the feed composition of Sty was kept to ~10 mol % while that of the CLA was kept below 16 mol %.

Peak Assignment

The univariate method is a straightforward calibration technique and because of its simplicity it should be attempted prior to the use of a multivariate method.¹⁴⁻¹⁶ In the univariate

approach to monitoring polymerizations, the absorbance of the different functional groups within the monomers or polymers are monitored. Each functional group is associated with a characteristic peak, and its concentration is assumed proportional to its absorbance according to Beer's law. This method was applied to a large population (107 spectra) of CLA/Sty, CLA/BA, and CLA/Sty/BA runs by tracking each characteristic peak height from each spectrum as a function of conversion. An example of such a spectrum is shown in Figure 1.

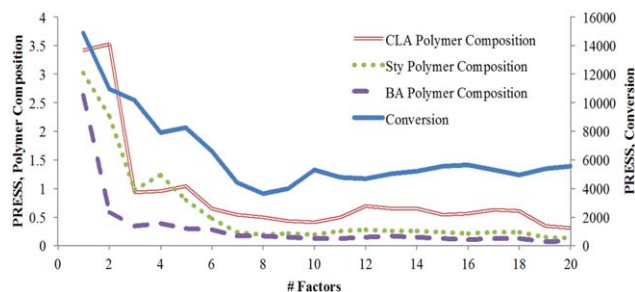


Figure 5. PRESS analyses for conversion and polymer compositions in bulk. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Each characteristic peak was evaluated for correlation between the IR peak height and the off-line conversion measurements; some peaks were observed to be strongly correlated. All of the identified peaks were validated with the literature for correct assignment to either the monomer or polymer of Sty, BA or CLA.^{19–22} The IR spectra of CLA, Sty, and BA monomers are shown, respectively, in Figures 2–4 and peak assignments are shown in Table II. For the emulsion polymerization experiments, it should be noted that the concentrations of CTA, AA, and DVB used were low enough that they did not interfere with the peak assignments. In addition, had they been at significant concentrations, one could perform a spectral subtraction to eliminate their contribution to the IR spectra.

As expected, the Sty and BA monomer peak heights trended down with conversion and the identified Sty and BA polymer peak heights trended up with conversion. When monitoring the CLA peaks, all the peak heights trended up with conversion indicating a probable overlap between monomer and polymer peaks. As a result of the above observations, a more complex

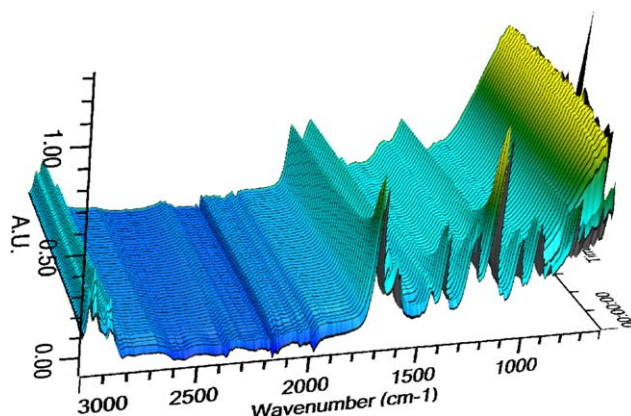


Figure 7. Example IR reaction spectra for CLA/Sty/BA: 8/10/82 mol/mol/mol feed composition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

multivariate calibration method was chosen for the IR monitoring of our reactions.

Multivariate Calibration Method for Bulk Polymerizations

A multivariate [partial least squares (PLS) regression] calibration was developed from 42 spectra selected from the bulk CLA/Sty, CLA/BA, and CLA/Sty/BA runs (see Table I). QuantIR software from ReactIR 45m (Mettler Toledo) was used to perform the analysis. With the PLS approach, a set of calibration spectra are reduced to a smaller number of key spectra (called factors) taken in a linear combination to approximate the original spectral data. Each of those factors is composed of multiple peaks within the same spectral region. A predicted residual error sum of squares (PRESS) analysis is used to select the optimum number of factors for each component (composition or conversion). As factors that represent useful information are added to

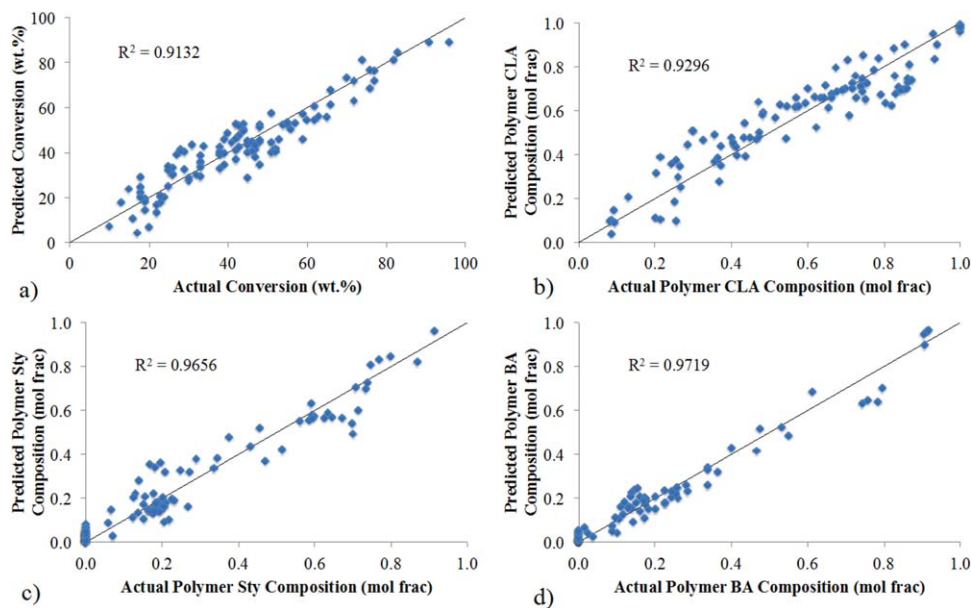


Figure 6. PLS predictions for bulk polymerizations: (a) overall conversion, (b) CLA polymer composition, (c) Sty polymer composition, and (d) BA polymer composition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

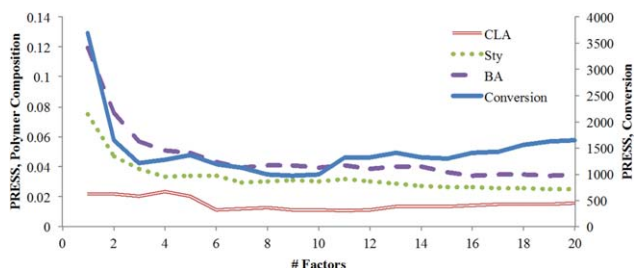


Figure 8. PRESS analyses for conversion and polymer composition in emulsion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the analysis, the PRESS value decreases, indicating improvement in the PLS calibration error. At some point, the factors add unnecessary information and the PRESS value levels off or increases. The correct number of factors to select is associated to the initial levelling off point.

For the bulk polymerizations, the entire spectral region was chosen for the PRESS analyses performed on both conversion and polymer composition data. The optimum number of factors was chosen (as suggested by the QuantIR software) as eight for all four calibration models (i.e., overall conversion, and CLA, Sty, and BA polymer compositions) and those results are shown in Figure 5.

The PLS models were built to establish a predictive relationship between the factors and the off-line gravimetric and $^1\text{H-NMR}$ measurements. Out of the 107 spectra available for these analyses, 42 were used for calibration (or training as it is referred to by the QuantIR software) and 65 were used for validation (or testing). Each of the four models was successfully calibrated and validated using the same set of spectra. Model predictions versus off-line data are shown in Figure 6 for conversion, and

CLA, Sty, and BA polymer compositions. All of the data used for calibration as well as for validation are included in Figure 6.

A paired comparison was carried out between the model predictions and the actual data. About 95% confidence intervals for the difference between the off-line and ATR-FTIR data were found to include zero for all four models, indicating that no significant differences existed. The 95% confidence intervals were $[-1.71, 0.80]$ (wt %) for conversion, $[-0.0125, 0.0208]$ (mole fraction) for CLA polymer composition, $[-0.0116, 0.0132]$ (mole fraction) for Sty polymer composition, and $[-0.0133, 0.0033]$ (mole fraction) for BA polymer composition.

Multivariate Calibration Method for Emulsion Polymerizations

As was the case for the bulk polymerizations, univariate calibration was attempted for the CLA/Sty/BA emulsion terpolymerizations and yielded similar results. Thus, the PLS calibration was applied to the emulsion polymerization runs (see Table I). A total of 70 spectra were available for analysis. Figure 7 shows sample spectra for the duration of an emulsion terpolymerization. The PRESS analysis (see Figure 8) suggested the use of nine factors for all four calibration models (i.e., overall conversion, and CLA, Sty, and BA polymer compositions). Out of the 70 spectra used in these analyses, 55 were used for calibration (or training) and 15 were used for validation (or testing). All four models were successfully calibrated using the same set of spectra. Model predictions versus off-line data are shown in Figure 9 for conversion, and CLA, Sty, and BA polymer compositions. It should be noted that all of the data used for both calibration and validation are included in Figure 9. It is worth commenting on the R^2 values in Figure 9 (and comparing to those in Figure 6). One should recall that R^2 values reflect goodness of fit to a “straight line” model. In some instances in Figure 9, plots with low amounts of scatter in the data have relatively low R^2 values; this reflects slight non-linearity in the

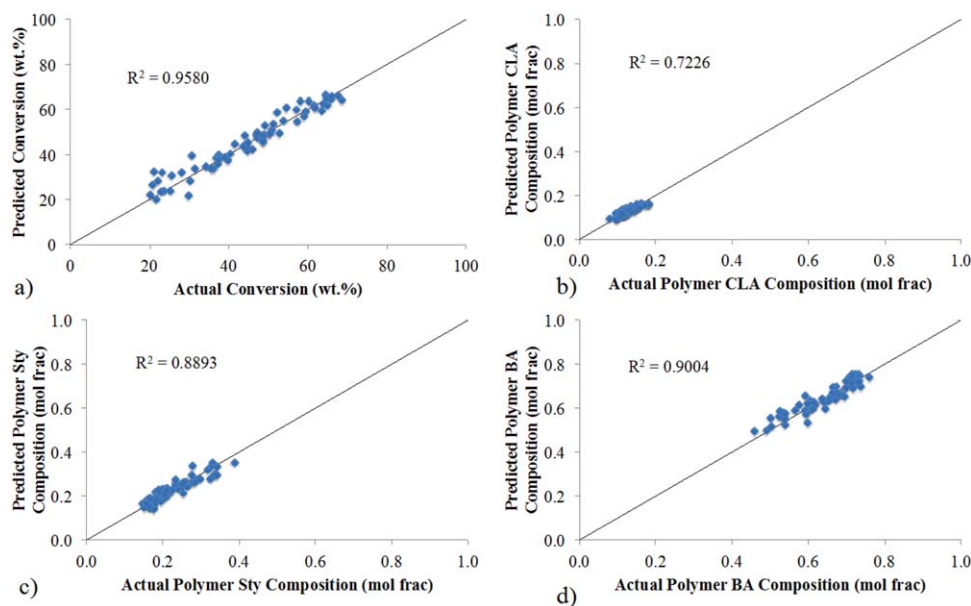


Figure 9. PLS predictions for emulsion polymerizations: (a) overall conversion, (b) CLA polymer composition, (c) Sty polymer composition, and (d) BA polymer composition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

data as opposed to a high variance or scatter. The narrow range of data and small sample size [e.g., see Figure 9(b)] would also negatively influence the R^2 value.

As in the case for the bulk polymerizations, paired comparisons were carried out between the model predictions and the off-line data. The 95% confidence intervals for the difference between the calibration model and the off-line data were found to include zero for all four models, indicating that no significant differences existed. The 95% confidence intervals are [-0.44, 1.18] (wt %) for overall conversion, [-0.0028, 0.0030] (mole fraction) for CLA polymer composition, [-0.0063, 0.0041] (mole fraction) for Sty polymer composition, and [-0.0051, 0.0072] (mole fraction) and for BA polymer composition.

Another valuable consequence of in-line data collection is driven home in Figure 7. One notes that, in Figure 7, two large peaks at $\sim 1190\text{ cm}^{-1}$ and at $\sim 1730\text{ cm}^{-1}$ increased quickly during the first 5–10 min of the reaction, and then decreased. These changes were rapid enough to make the monitoring of the true trajectory via off-line sampling difficult. According to our peak assignments, both of these peaks relate to both CLA polymer and BA monomer, i.e., the CLA polymer and BA monomer peaks overlap at both 1190 cm^{-1} and 1730 cm^{-1} (refer to Table II). This trajectory confirms earlier speculation on the behavior of the oleic acid impurity found in the CLA.^{11–13} An initial production of CLA-rich oligomers is reflected by the sharp increase in the two peaks for the first 5–10 min. When the effect of oleic acid, acting as an impurity, has abated, the consumption of BA monomer then causes the decrease of those same peaks due to their overlapping functional groups with that of the CLA polymer. Of course, if the peaks were strictly assigned to a monomer, one would expect the peaks to reach an absorbance near zero. In Figure 7, that is clearly not the case and the peaks level off due to the produced CLA polymer (oligomers). It should be added that the oleic acid and saturated fatty acid peak assignments overlap with that of the CLA. As the oleic acid and saturated fatty acid are not consumed, the peaks associated to these should not be affected.

CONCLUSIONS

The successful off-line and in-line monitoring of bulk and emulsion CLA/Sty/BA co- and terpolymerizations was achieved. The calibration models were validated using off-line data and no significant differences between the ATR-FTIR results and the off-line data were found. Beyond simply monitoring these polymerizations, the in-line monitoring method provided an interesting confirmation of the reaction kinetics. This kinetic observation demonstrates the value of a continuous in-line monitoring procedure when fast kinetics precludes the ability to monitor a reaction using intermittent, costly, and time-consuming off-line measurements.

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