

# **Application of Online FT-NIR Spectroscopy to Study the Kinetics of Anionic Polymerization of Butadiene**

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## **Abstract**

Online Fourier-transform near infrared (FT-NIR) spectroscopy in combination with a fiber optic probe was successfully utilized to study the kinetics of the anionic polymerization of butadiene. The conversion of the butadiene to methylene protons in the polymer was easily monitored in solution polymerization conditions. Butadiene polymerization kinetics was investigated in cyclohexane with n-butyl lithium as initiator. A kinetic expression was obtained for the polymerization of butadiene in cyclohexane initiated with n-butyllithium.

## Introduction

Growing interest on product prepared by anionic polymerization techniques has been used industrially during the last three decades. In order to understand the mechanisms for these processes, kinetics investigations are of special interest since they could help us to have a better control during the industrial synthesis of polymers. There are many techniques to determine the conversion profiles of polymerizations. Recently, online techniques like FT-NIR spectroscopy were used to monitor polymerization processes. One of the major advantages of this technique is that sampling and post-processing of the samples, the most consuming time steps, can be avoided. The monitoring of anionic polymerization of styrene, isoprene and methyl methacrylate by FT-NIR online was reported in the literature. Since in the rubber industry is interested in the controlled synthesis and application of homopolymers and block copolymers we were considering FT-NIR as an inexpensive tool to for monitoring the conversion of the monomers in the polymerization reactor. In this paper we show that in the FT-NIR, specific signals of various monomers can be used for monitoring the conversion of the butadiene without the use of chemometric methods. A kinetic expression for the anionic polymerization of butadiene in cyclohexane is reported.

## Methods

Cyclohexane was purified by distillation and was kept under dry nitrogen atmosphere before usage. Butadiene (Repsol-YPF) was passed over columns packed with molecular sieve and activated alumina and n-butyllithium (FMC) was used as received. Polymerizations were carried out at different temperatures in a 20 l reactor. The NIR probe was connected to the reactor using a bypass. NIR spectra were measured using a FOSS 6500 scanning spectrophotometer (FOSS) which is equipped with an optical probe.

## Results and Discussion

The NIR spectrum of butadiene after solvent subtraction reveals that at the characteristic absorbance at 1632 nm should be suitable for the determination of butadiene conversion. This absorbance has been assigned to the two pairs of vinyl carbon-hydrogen bonds ( $H_2C=C$ ) in the butadiene.

Conversions were calculated using the following equation:

$$\%X(t) = \left( \frac{A_{1632}(0) - A_{1632}(t)}{A_{1632}(0) - A_{1632}(\infty)} \right) * 100,$$

where  $A_{1632}(0)$  is the initial absorbance at 1632 nm,  $A_{1632}(t)$  is the absorbance at time  $t$ , and  $A_{1632}(\infty)$  is the absorbance at full conversion of the butadiene.

The time conversion plot is shown in Figure 1. A comparison with GPC data reveals the excellent agreement between both methods.

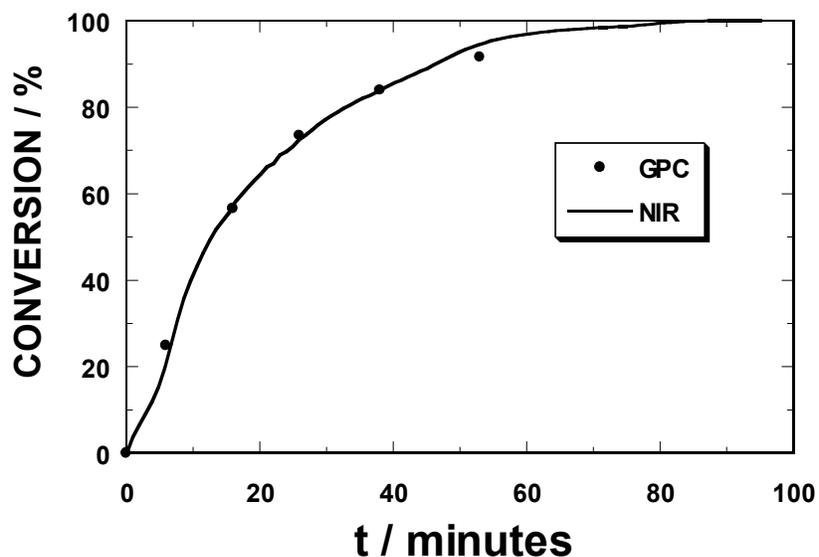


Figure 1. Time-conversion plot for the polymerization of butadiene. Comparison of GPC data and real-time FT-NIR monitoring at 1632 nm.

In the Figure 2 is shown the time-conversion plot for the polymerization of butadiene for different n-butyllithium concentrations. The polymerizations were performed at 60 °C.

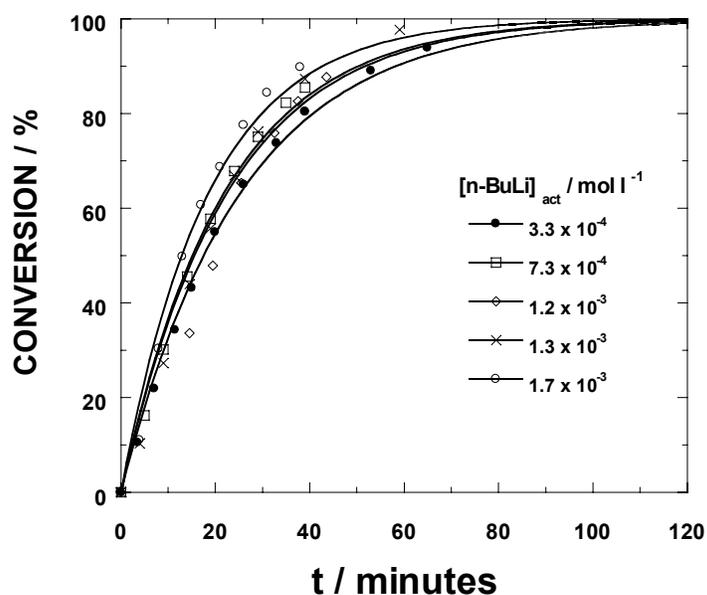


Figure 2. Time-conversion plot for the polymerization of butadiene for different initiator concentrations.

We used a first order model in order to obtain the apparent constant of polymerization. Figure 3 shows the apparent constant of polymerization in function of the active concentration of n-butyllithium.

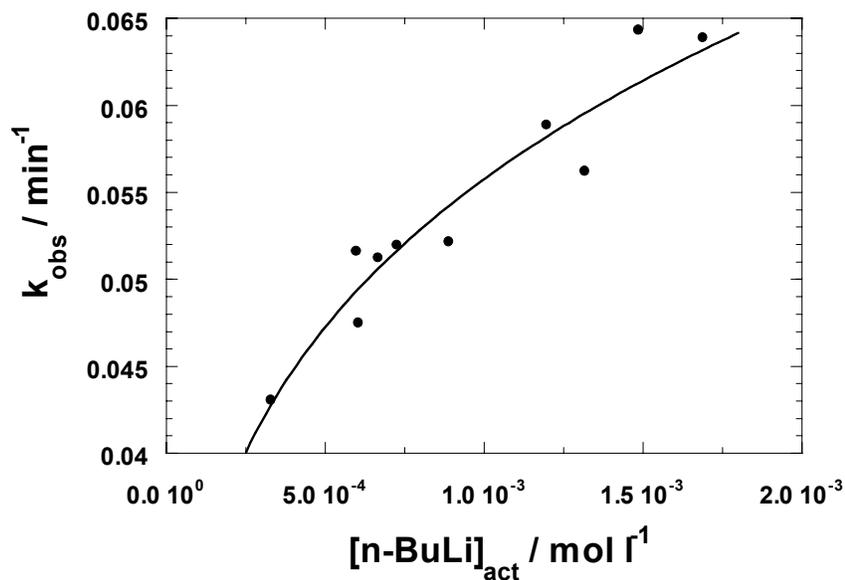


Figure 3. Apparent constant of polymerization as a function of the concentrations of n-butyllithium.

The order respect to the concentration of active n-butyllithium was 0.24. This is very close to the order reported by other authors, 0.25, for the propagation step in the anionic polymerization of the butadiene initiated with n-butyllithium in cyclohexane.

In the Figure 4 is shown the time-conversion plot for the polymerization of butadiene for at different temperature. The concentration of active n-butyllithium was kept constant in

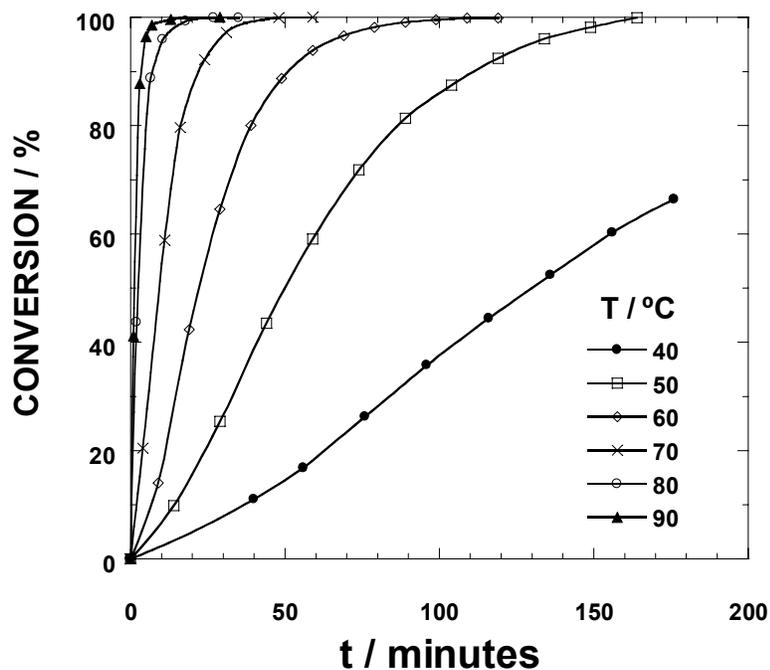


Figure 4. Time-conversion plot for the polymerization of butadiene at different temperatures.

We used a first order model in order to obtain the apparent constant of polymerization. Figure 5 shows an Arrhenius plot for the anionic polymerization of butadiene in cyclohexane using n-butyllithium as initiator.

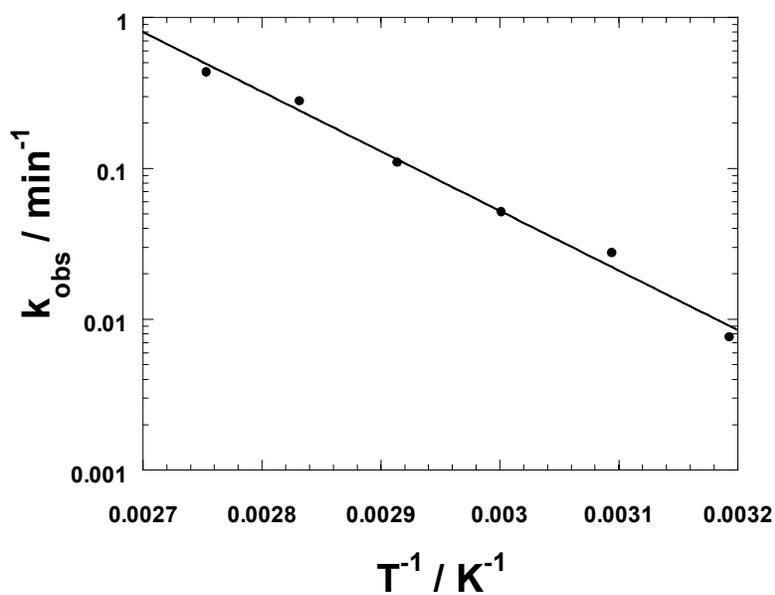


Figure 5. Arrhenius plot for the anionic polymerization of butadiene.

Finally, we obtained a kinetic expression for the anionic polymerization of butadiene in cyclohexane using n-butyllitium, NBL, as initiator.

$$R_p = -\frac{d[Bd]}{dt} = 2.14 \times 10^{11} \exp\left\{-\frac{9097.4}{T}\right\} [NBL]_0^{0.24} [Btd].$$

This expression was used to predict the kinetic data reported in the literature for other authors. The kinetic data were obtained under different conditions than the used in this study. In the Figures 6 and 7, we compare the predictions obtained with kinetic expression with the kinetic data reported in the literature.

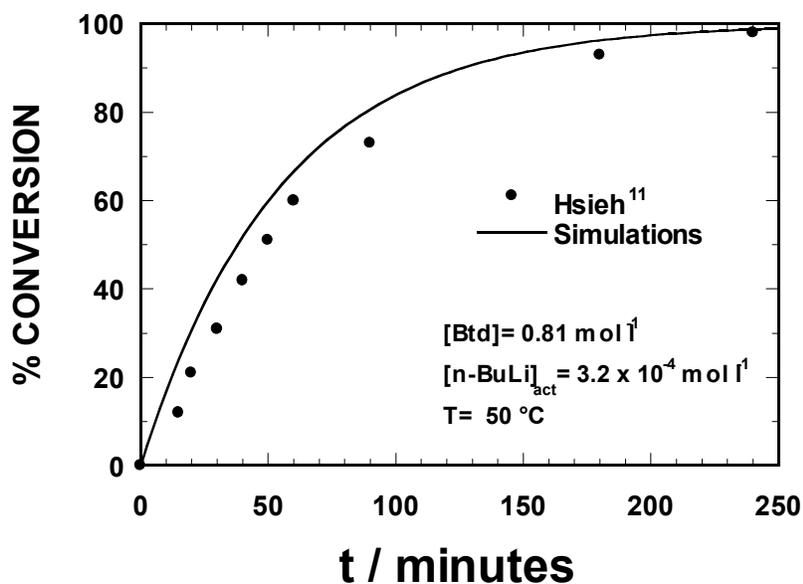


Figure 6. Comparative between predictions obtained with the kinetic expression and kinetic data reported in the literature.

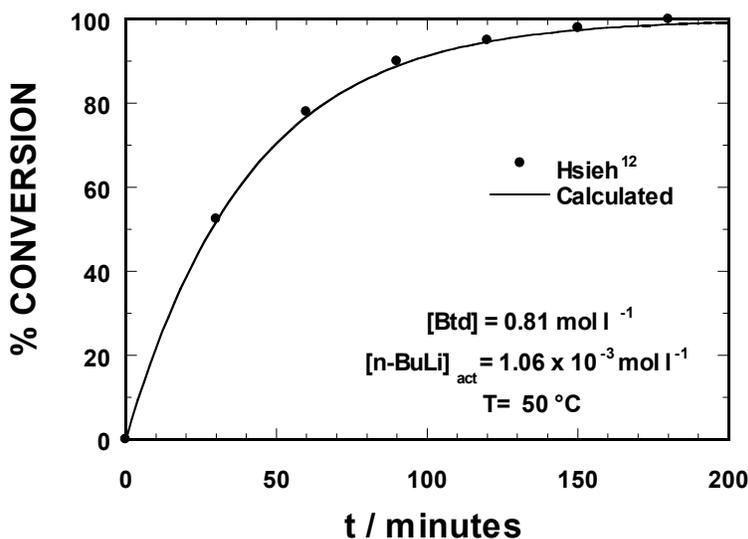


Figure 7. Comparative between predictions obtained with the kinetic expression and kinetic data reported in the literature.

The kinetic expression predicts properly the kinetic data obtained at different conditions that the used in this paper.

## Conclusions

Online FT-NIR spectroscopy in combination with a fiber optic probe was successfully used to monitor the anionic polymerization of butadiene. The kinetic data obtained were used in order to get an analytical expression for the anionic polymerization of butadiene. The predictions obtained with the kinetic expression were compared

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