

Mid-IR real-time monitoring of the carbocationic polymerization of isobutylene and styrene

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Summary

The *in-situ* monitoring of the living carbocationic polymerization of isobutylene (IB) and styrene (St) with a fiber optic Attenuated Total Reflection (ATR) probe in the mid-IR “fingerprint” range is reported here for the first time. Monomer consumption was followed by the disappearance of the C = C stretching for both IB and St, and the C - H bending of the CH₃ group in IB. The formation of polyisobutylene (PIB) was also monitored by tracing the asymmetrical doublet characteristic of C - H bending of the t-butyl groups of the PIB. Conversion measurements by conventional off-line gravimetry correlated well with the new technique.

Introduction

The living carbocationic polymerization of olefins is a relatively recent development, leading to the synthesis of well-defined macromolecules such as high molecular weight (MW) PIBs with narrow molecular weight distribution (MWD), or PIB-based thermoplastic elastomeric block copolymers, that were unavailable before (1,2). The kinetics and mechanism of the living carbocationic polymerization of IB are controversial and debated in the literature (1,3-5). It was therefore a desirable objective to find an experimental technique suitable for the *in-situ* monitoring of these polymerizations. Near-infrared (NIR) spectroscopy combined with a fiber optic probe was used successfully to monitor living anionic processes (6). However, the NIR bands are overtones or combinations of fundamental bands, which makes them difficult to identify and they usually overlap. NIR techniques therefore must use multivariable calibration procedures and/or Partial Least Square PLS fitting methods for spectra evaluation. The mid-IR, with its fundamental bands, was expected to be a more suitable method, but no relevant reference was found in the literature. This report describes the first example of *in-situ* monitoring of the carbocationic polymerization of IB and St in the mid-IR range.

Experimental

Materials

Methyl chloride (MeCl) and IB were condensed from the gas phase. Methyl cyclohexane (MeCHx) (Phillips, polymerization grade) and THF (Baker, HPLC grade) were distilled off CaH₂. St was purified by chromatography to remove the inhibitor followed by vacuum

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distillation. 2-chloro-2,4,4-trimethylpentene (TMPCl) was synthesized as reported (7). Titanium tetrachloride (TiCl_4), di-*t*-butylpyridine (DtBP) and methanol were used as received.

Procedures

Polymerizations were carried out in round-bottomed flasks equipped with an overhead stirrer in a dry box under a dry nitrogen atmosphere. The flask was charged with MeCHx and MeCl (60/40 v/v mixture), TMPCl (0.002 mol/L), DtBP (0.007 mol/L) and the monomer (IB = 2 mol/L; St = 1 mol/L) and the charge was cooled down to -80°C . The fiber optic ATR immersion probe (Remspec Inc., shown in Figures 1 and 2), interfaced

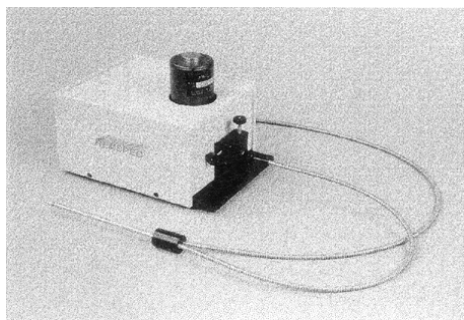


Figure 1. Mid-IR detector module

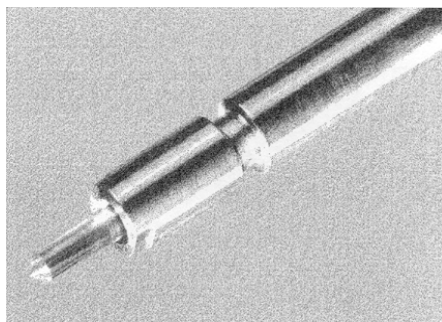


Figure 2. Fiber optic ATR immersion probe

with a Bio-Rad FTS 175C FTIR unit, was fed into the dry box through a port and immersed into the reaction mixture. Background scans were taken after the addition of each ingredient. Polymerizations were started with the addition of TiCl_4 (0.037 mol/L). Scans were taken every 6 seconds and the data were collected and evaluated by the Bio-Rad Win-IR kinetic software. Samples were taken at specified times into chilled culture tubes containing methanol for parallel gravimetric conversion measurement and SEC characterization. MWs and MWDs were determined by Size Exclusion Chromatography (SEC) using a Waters system equipped with 6 Ultrastaygel columns (100, 500, 10^3 , 10^5 and 10^6 Å) thermostatted at 35°C . The mobile phase was THF at 1 ml / min flow rate. The flow rate was monitored by the use of elemental sulfur as the internal marker. The instrument was calibrated with 14 narrow MWD PSt standards. MW and MWD values for PIBs were calculated using the Universal calibration principle, which was demonstrated to give excellent agreement with narrow PIB calibration (8).

Results and discussion

Figure 3 shows the real time plots for the disappearance of the 1655 cm^{-1} band characteristic of the C = C stretching in IB. Figure 4 shows the real-time disappearance of the 1375 cm^{-1} band characteristic of the C-H stretching in the CH_3 -group of IB, and the real-time appearance of the asymmetrical doublet at 1365 and 1390 cm^{-1} representing the C-H stretching bands of the *t*-butyl groups of the forming PIB.

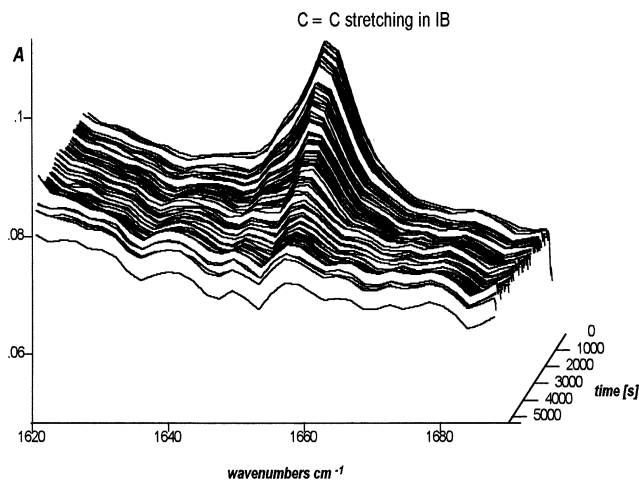


Figure 3:
Real-time IR-plots

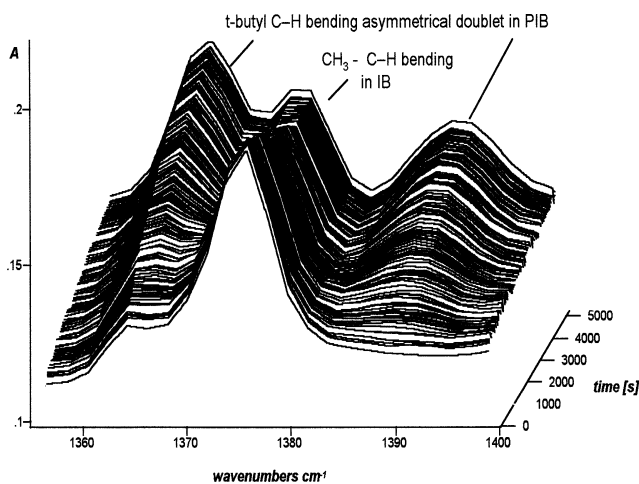


Figure 4:
Real-time IR-plots

It is also apparent from Figures 3 and 4 that the mid-IR signals are strong and can easily be identified. Figure 5 shows the conversion-time plot obtained by tracing the area under the 1655 cm^{-1} band, assuming that the IB concentration is proportional to the peak area. Figure 6 presents the conversion-time plots tracing the peak heights as displayed in Figure 4, assuming that the corresponding peak heights are proportional to the concentration of IB and PIB, respectively. The agreement between the conventional and the fiber optic method is excellent when the peak area is used (see Figure 5), and good even with the peak heights (Figure 6). Figure 7 displays the comparison of conversion-time plots for a St polymerization obtained by conventional gravimetry and by tracing the area under the 1630 cm^{-1} band characteristic of the C = C stretching in St; the agreement

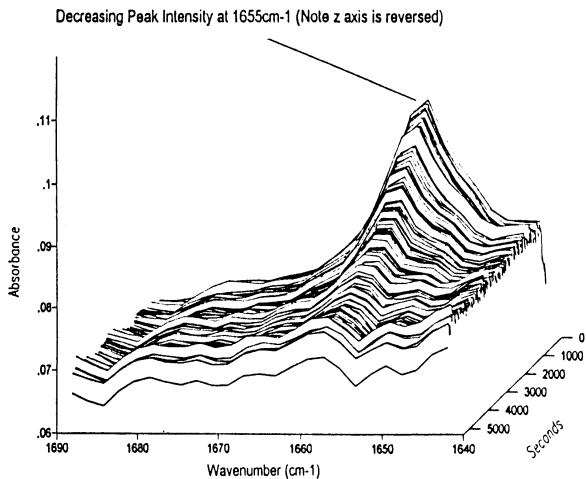


Figure 3.
Real-time
IR-plots

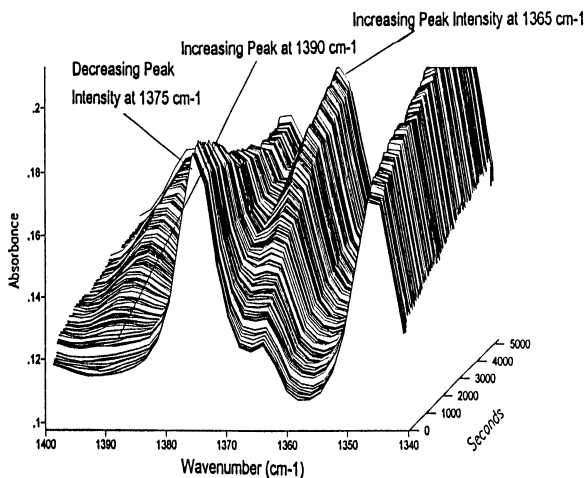


Figure 4.
Real-time
IR-plots

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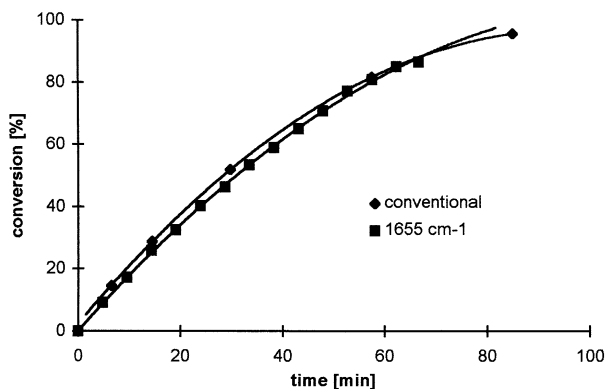


Figure 5.
Conversion-time plots
for IB
polymerization

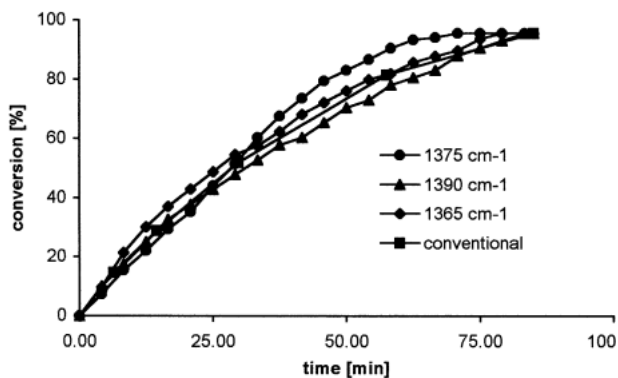


Figure 6.
Conversion-time plots
for IB
polymerization

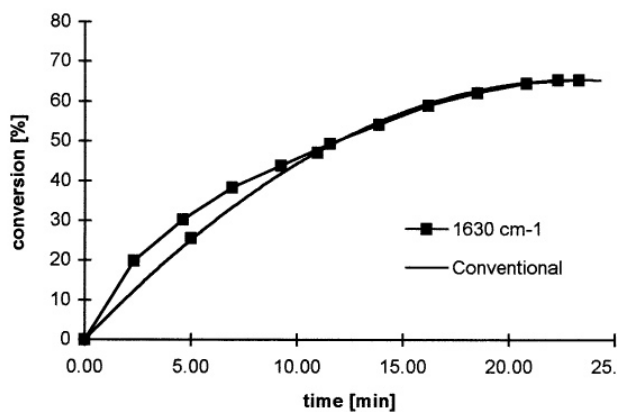


Figure 7.
Conversion-time plots
for a St
polymerization

is very good. The results discussed demonstrate that this technique seems to be very powerful for the in-situ monitoring of IB and other solution polymerizations. Figure 8 shows the linear $\ln [M]_0/[M]_t$ - time plot constructed for the IB polymerization at low conversions. Using the kinetic model developed for living IB polymerizations (3), the slope of the line yielded an apparent rate constant of propagation $k_p' = 6.6 \text{ L}^2/\text{mol}^2\text{sec}$. This parameter was used to predict the MWD by the Predici© polyreaction simulation package (CIT, Germany). Figure 9 shows the comparison of simulated and measured MWDs; the agreement is very good. The final MW of the PIB was $\overline{M}_n = 60,000$ and the \overline{M}_n increased linearly with conversion. The details of kinetic investigations of living IB polymerizations will be discussed elsewhere (9).

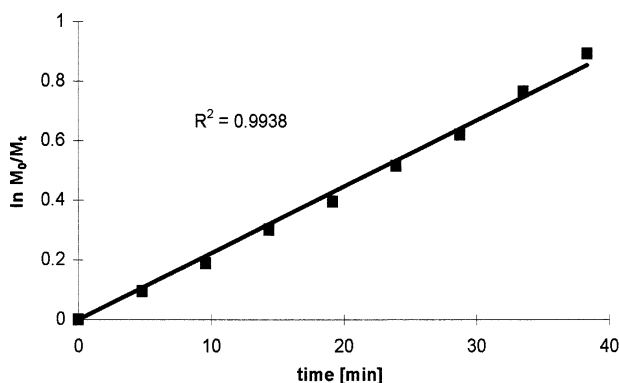


Figure 8.
 $\ln [M]_0/[M]_t$ -
time plot
for the IB
polymerization

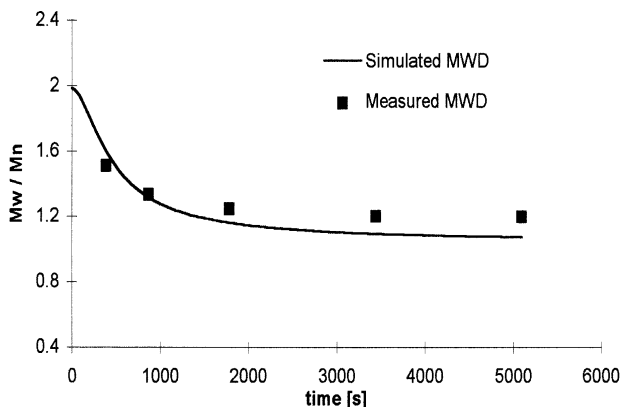


Figure 9.
Comparison
of simulated
and measured
MWDs

In sum, the Remspec immersion ATR probe in conjunction with a Bio-Rad FTIR instrument was demonstrated to be suitable for the real-time monitoring of the carbocationic polymerization of IB and St. Further development of this technique is in progress.

Acknowledgements

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