

APPLICATION OF FT-NIR SPECTROSCOPY FOR MONITORING THE KINETICS OF LIVING POLYMERIZATIONS

Michael Lanzendörfer, Holger Schmalz, Volker Abetz, Axel H. E. Müller*

Makromolekulare Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany

Introduction

Fourier-transform near infrared (FT-NIR) fiber optic spectroscopy was successfully used to monitor the living cationic polymerization of isobutylene (IB), the anionic polymerization of ethylene oxide (EO), and the Atom Transfer Radical Polymerization of *t*-butyl acrylate (tBA). After the development of online monitoring techniques for the living anionic polymerizations of styrene (S) and isoprene in the near infrared range¹, methods were developed that allow to follow the polymerization of IB^{2,3} and S^{2,4} in the mid-infrared (MIR) range. It was believed that NIR could not be used due to overlapping signals. In this paper we show that even in the NIR specific signals of the monomer can be used for monitoring conversion without using deconvolution methods in IB as well as EO polymerizations.

Experimental

Materials. Tetrahydrofuran (Merck) and *n*-hexane (Merck) were purified by successive distillation over CaH₂ and Na/K (hexane) or K (tetrahydrofuran) and kept under dry nitrogen before usage. Dichloromethane was refluxed over CaH₂ under dry nitrogen. IB was dried by passing over a drying column (LabClear, Aldrich) before condensation from the gas phase. Ethylene oxide (Linde) was condensed onto CaH₂ and stirred at 0 °C for 3 h before being transferred into glass ampoules. 2-Chloro-2,4,4-trimethylpentane (TMPCl) was prepared from 2,4,4-trimethyl-1-pentene by hydrochlorination and purified by distillation. 2,6-Di-*t*-butylpyridine (DtBP, Aldrich), TiCl₄ (Aldrich), the phosphazene base *t*-Bu-P₄ (Fluka, 1 M in hexane) and *sec*-BuLi (Acros, 1.3 M in cyclohexane/hexane: 92/8) were used as received.

Equipment. NIR spectra were recorded with a Nicolet Magna 560 FT-IR optical bench equipped with a white light source and a PbS detector. Online monitoring was accomplished using a laboratory autoclave (Büchi) equipped with an all glass low temperature immersion transmission probe (Hellma) with an optical path length of 10 mm and connected to the FTIR by 2 m fiber-optical cables. The probe was fed through a port in the stainless steel top plate of the reactor and immersed into the reaction mixture. Data processing was performed with Nicolet's OMNIC Series software. Each spectrum was constructed from 32 scans with a resolution of 4 cm⁻¹. The total collection time per spectrum was about 22 s. Data collection was started 7 min before TiCl₄ addition.

Polymerizations. Polymerizations were carried out in a thermostated laboratory autoclave (Büchi) under dry nitrogen atmosphere. In the case of IB the reaction vessel was charged with solvents *n*-hexane/CH₂Cl₂ (2/1 v/v) followed by DtBP and TMPCl. The mixture was cooled to -78 °C and a background spectrum of 128 scans was taken before addition of IB. After adequate mixing the reaction was started by addition of TiCl₄ and quenched with methanol after complete conversion ([IB]₀ = 1 M, [TiCl₄] = 0.02 M, [TMPCl] = 4 mM, [DtBP] = 2 mM). Samples were taken at specified times into chilled sample tubes containing methanol for parallel gravimetric analysis.

EO polymerization was performed in THF solution using *sec*-BuLi as initiator along with the phosphazene base *t*-BuP₄.⁵⁻⁸ *sec*-BuLi was added to THF at -78 °C followed by addition of EO. After stirring for 30 min the reaction mixture was heated to 40 °C or 50 °C and the reaction was started by addition of *t*-BuP₄ ([*sec*-BuLi] = [*t*-BuP₄] = 2.34 · 10⁻³ M; [EO] = 0.53 M). Simultaneous gravimetric investigations were performed using septum-sealed flasks containing MeOH/AcOH (1/5 v/v) as termination agent. After complete conversion the reaction was terminated with a mixture of MeOH/AcOH (1/5 v/v).

Results and Discussion

Isobutylene. Fourier transform near infrared spectroscopy can be accomplished without expensive hardware. One of the authors' previous work dealt with MIR monitoring of IB polymerization using fiber-optic equipment.² It therefore seemed to be a desirable goal to combine the advantage of fiber optics with low-cost fibers available for measurements in the NIR range. The

NIR spectrum of IB obtained after solvent subtraction (Fig. 1) reveals at least three signals which should be suitable for the determination of monomer conversion. A fourth signal was detected close to the solvent cutoff around 4550 cm⁻¹. The signal at 6116 cm⁻¹ was assigned as the first overtone of the v_{as}(=CH₂) stretching, whereas the other signals at 4732, 4626 cm⁻¹ and below are combinations of fundamental vibrations of IB. The region between 6000 and 5500 cm⁻¹ is inaccessible due to solvent interference but is not expected to show any significant absorptions of IB as verified by gas phase spectra of IB.

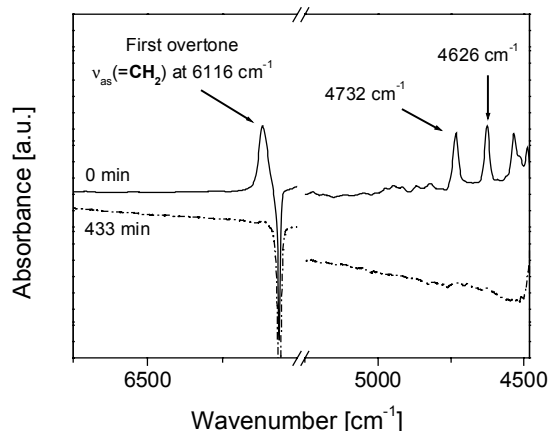


Figure 1. NIR spectra of IB in hexane/CH₂Cl₂ (2:1) at -78 °C obtained after solvent subtraction at *t* = 0 and at full conversion.

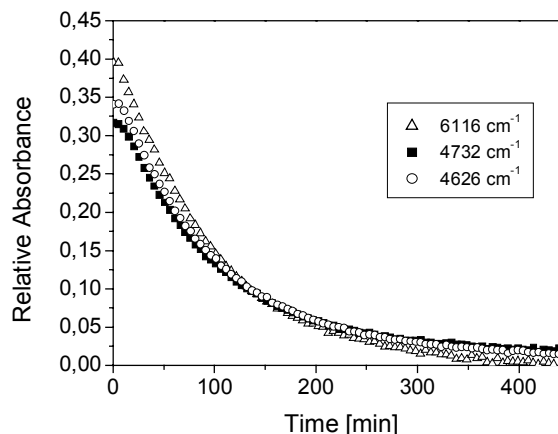


Figure 2. Real-time plot of peak heights in IB polymerization at various wave numbers.

Fig. 2 shows the decay of peak heights for these signals during the course of the reaction. Conversions were calculated using the following equation:

$$\text{conversion} = \frac{A_0 - A_t}{A_0 - A_\infty}$$

where A_t is the relative absorbance at time t , A_0 = initial absorbance and A_∞ = absorbance at full conversion.

The time-conversion plot is shown in Fig. 3. A comparison with gravimetric data reveals the excellent agreement between both methods. In contrast to measurements in the MIR, no signals from the formed polymer were detectable. This was expected, since polyisobutylene has no significant absorptions in the NIR.

Ethylene Oxide. Motivated by this result we began to look for non-vinyl monomers which could also be suitable for online monitoring by FT-NIR. Ethylene oxide (EO) is a hazardous toxic monomer but widely used in technical products (e.g. PluronicTM, cosmetics, medical applications). The online measurement of EO conversion during polymerization with Li⁺/*t*-BuP₄ is also of academic interest since only one report is available that deals with kinetic data of this system.⁶ This specific report was slightly confusing concerning the reaction conditions under which these data were received. It would therefore be helpful to have a valuable non-destructive tool for determination of additional kinetic data. In order to check the applicability we recorded an NIR spectrum of pure EO in THF using background subtraction (see Fig. 4). EO shows specific monomer signals at 6070 and 4548 cm⁻¹ that can be attributed to combinations of fundamental vibrations.⁹ The latter signal is too close to the solvent cutoff and was therefore not used for conversion determination. The region between 6000 and 5400 cm⁻¹ is inaccessible due to solvent interference but shows no monomer signals.^{9,10}

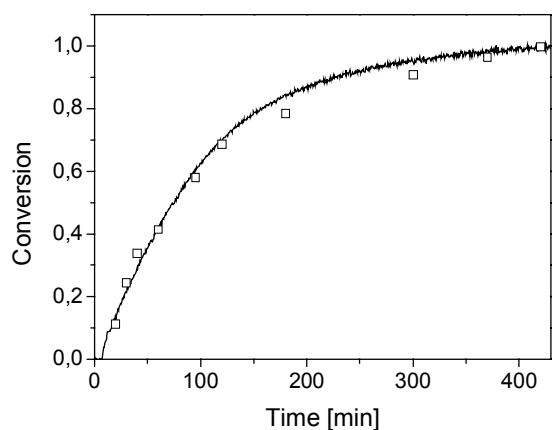


Figure 3. Time-conversion plot in IB polymerization. Comparison of gravimetric data (□) and real-time FT-NIR monitoring at 6116 cm⁻¹.

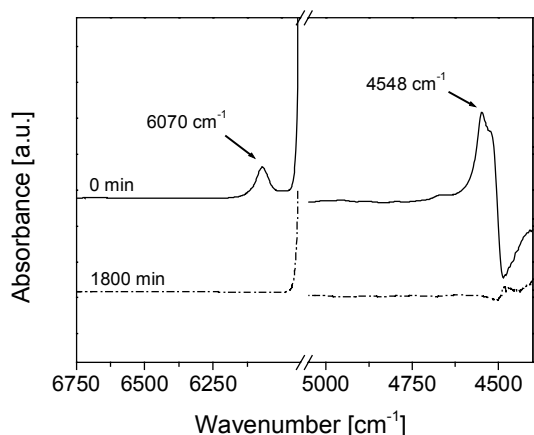


Figure 4. NIR spectra of EO in THF at 50 °C obtained after solvent subtraction at *t* = 0 and at full conversion.

Fig. 5 shows the linear and first-order time-conversion plots that were constructed with the NIR data and compared to gravimetric measurements, exhibiting excellent agreement between both methods for this monomer. Unexpectedly, we observed a long induction period of the polymerization under our reaction conditions, whereas no induction period was found when potassium naphthalide is used as initiator. When increasing the temperature from 40 °C to 50 °C the polymerization rate increased and the induction period decreased. Once the polymerization had started, a linear first-order dependence in monomer concentration was found for both temperatures. At

this point we are not able to explain this behavior and further experimental data are needed for mechanistic interpretations.

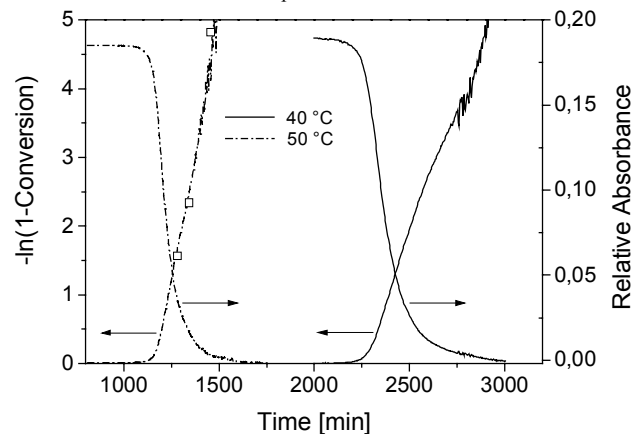


Figure 5. Linear and first-order time-conversion plots in EO polymerization at two reaction temperatures indicating long induction periods. For comparison, gravimetric data (□) are given for the reaction at 50 °C.

***tert*-Butyl acrylate.** We also were able to follow the atom transfer radical polymerization (ATRP) of *tert*-butyl acrylate (tBA) in acetone at 45 °C at 50 % initial monomer concentration. These results will be reported elsewhere.¹¹

Conclusions

FT-NIR spectroscopy in combination with a fiber-optic low temperature probe was successfully used to monitor living IB and EO polymerizations using specific monomer absorptions. In the case of EO a temperature dependent induction period was detected when *sec*-BuLi and *t*-BuP₄ were used as an initiating system.

References

- (1) Long, T. E.; Liu, H. Y.; Schell, B. A.; Teegarden, D. M.; Uerz, D. S. *Macromolecules* **1993**, *26*, 6237-6242.
- (2) Puskas, J. E.; Lanzendörfer, M. G.; Pattern, W. E. *Polym. Bull.* **1998**, *40*, 55-61.
- (3) Storey, R. F.; Donnalley, A. B.; Maggio, T. L. *Macromolecules* **1998**, *31*, 1523-1526.
- (4) Storey, R. F.; Maggio, T. L.; Brister, L. B. *ACS Div. Polym. Chem., Polym. Preprs.* **1999**, *40*, 964-965.
- (5) EBwein, B.; Möller, M. *Angew. Chem.* **1996**, *108*, 703-705.
- (6) EBwein, B.; Molenberg, A.; Möller, M. *Macromol. Symp.* **1996**, *107*, 331-340.
- (7) EBwein, B.; Steidl, N. M.; Möller, M. *Macromol rapid Commun.* **1996**, *17*, 143-148.
- (8) Förster, S.; Krämer, E. *Macromolecules* **1999**, *32*, 2783-2785.
- (9) Linnett, J. W. *J. Chem. Phys.* **1938**, *6*, 692-702.
- (10) Bonner, L. G. *J. Chem. Phys.* **1937**, *5*, 704-706.
- (11) Cheng, G.; Lanzendörfer, M.; Müller, A.H.E. in preparation.