Macromolecules **1998,** *31,* 1523−1526

Real-Time Monitoring of Carbocationic Polymerization of Isobutylene Using in Situ FTIR-ATR Spectroscopy with Conduit and Diamond-Composite Sensor Technology

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Received August 27, 1997; Revised Manuscript Received December 31, 1997

ABSTRACT: Isobutylene (IB) polymerization kinetics were monitored in real time using mid-infrared FTIR-ATR spectroscopy, with a diamond-composite insertion probe and light conduit technology. Polymerization was initiated using the 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene (*t*-Bu-*m*-DCC)/2,4-dimethylpyridine (DMP)/$TiCl_4$ (1:2:20) system in hexane/methyl chloride (60:40 v/v) cosolvents at −80 °C, with [*t*-Bu-*m*-DCC] = 1.90×10^{-3} M and $[IB]_0 = 1.0$ M. Monomer concentration as a function of time was obtained by monitoring the absorbance at 887 cm^{-1} associated with the $=CH_2$ wag of IB. The calculated apparent first-order rate constant of 8.4×10^{-4} s^{-1} was within 3% of the value determined from traditional gravimetric methods (8.6×10^{-4} s^{-1}) withing the same range of conversion. Inspection of the first-order plot generated from the FTIR data revealed a number of deviations from linearity, which were attributed primarily to a transient rise and subsequent fall in reactor temperature caused by the initial large exotherm of polymerization. An artifact associated with the method of data analysis was also identified. These small differences in instantaneous rate were not detected by the gravimetric method due to insufficient accuracy and density of data points.

Introduction

The development of a complete understanding of the mechanism and kinetics of the living cationic polymerization of isobutylene (IB) is of great import for the production of novel materials[1−3] based upon this unique monomer. Numerous efforts have been undertaken in the last 20 years, but a complete understanding of this system has yet to be achieved.[4−10] This is due in large part to the extremely low concentration of active polymerization centers, the complicated role of system additives, and the absence of a sensitive, accurate, facile method of monitoring polymerization kinetics.

Traditional kinetic investigations of the polymerization of IB have been limited to gravimetric analysis of monomer consumption through a laborious, time-consuming process, which is experimentally limited to measurements below 5 half-lives and becomes increasingly more difficult to perform with increasing reaction rate. Recent efforts have focused on the development of a method for experimentally determining polymerization kinetics via in situ, real-time reaction monitoring utilizing mid-infrared FTIR spectroscopy employing a ReactIR 1000 reaction analysis system with a DiComp (diamond-composite) insertion probe (ASI Applied Systems, Millersville, MD) and real-time temperature logging.

The current investigation compares kinetic data for the 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene (*t*-Bu-*m*-DCC)−2,4-dimethylpyridine (DMP)−$TiCl_4$ initiating system (1:2:20) in hexane/methyl chloride (MeCl) (60:40 v/v) cosolvents for $[IB]_0 = 1.0$ M with [*t*-Bu-*m*-DCC] = 1.90×10^{-3} M at −80 °C, obtained by the traditional gravimetric method[11] vs direct in situ monitoring.

Experimental Section

Materials. The source and preparation of all reagents have been previously reported.[11]

Instrumentation. Molecular weights and molecular weight distributions were determined using a gel permeation chromatography (GPC) system equipped with a Wyatt Technology miniDAWN on-line MALLS detector, as previously described.[12] A ReactIR 1000 reaction analysis system (light conduit type) (ASI Applied Systems, Millersville, MD) equipped with a DiComp (diamond-composite) insertion probe, a general purpose type PR-11 platinum resistance thermometer (RTD), and a CN76000 series temperature controller (Omega Engineering, Stamford, CT) was used to collect infrared spectra of the polymerization components and monitor reactor temperature in real time.

Procedures. Polymerizations were carried out under dry nitrogen gas in a MBraun Labmaster 130 glovebox, equipped with an integral heptane bath cooled by both a FTS RC210 recirculating chiller (FTS Systems, Stone Ridge, NY) and liquid nitrogen, the latter regulated by a CN76000 series temperature controller (Omega Engineering, Stamford, CT). The polymerization procedure was as follows: the DiComp probe was inserted into a 2 L three-neck round-bottom flask, which was allowed to equilibrate in the −80 °C heptane bath prior to acquisition of a background spectrum (reactor atmosphere temperature ∼−60 °C). To the chilled flask, equipped additionally with a mechanical stirrer and RTD, were added sequentially 600 mL of hexane, 2.06×10^{-3} mol of *t*-Bu-*m*-DCC, 400 mL of MeCl, and 4.13×10^{-3} mol of 2,4-DMP. The reaction mixture was stirred until the solution reached thermal equilibrium as indicated by the RTD, and was then allowed to stir for an additional 10 min. Subsequently, 1.09 mol of chilled IB (−80 °C) was added to the reaction mixture, which was allowed to reach thermal equilibrium. After the reaction was stirred for an additional 10 min, 4.12×10^{-2} mol of $TiCl_4$ (neat and at room temperature) was rapidly injected into the reactor. The ReactIR 1000 was used to collect reaction temperature data and IR spectra for the entire premixing and reaction periods. Each spectrum was the Fourier transformation of 128 acquisitions collected over the spectral ranges 4000−2200 and 1900−650 cm^{-1}, within a time period of less than 1 min and with an instrument resolution of 8 cm^{-1}.

S0024-9297(97)01293-X CCC: $15.00

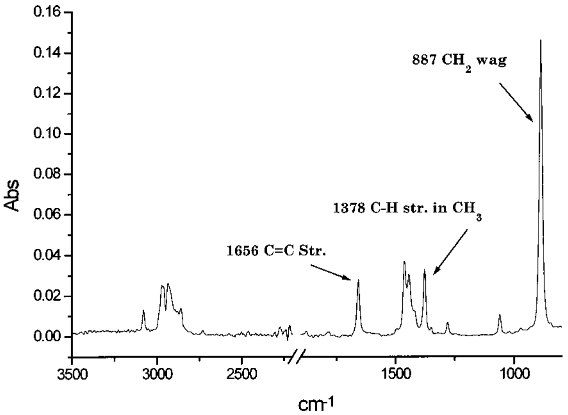

Figure 1. Pure-component FTIR spectrum of isobutylene obtained by solvent subtraction. The region below approximately 1000 cm^{-1} is inaccessible to traditional fiber optic probe technologies.

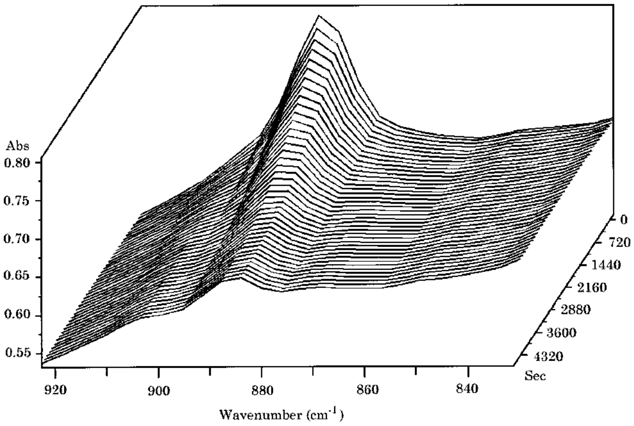

Figure 2. Real-time FTIR waterfall plot of the =CH$_2$ wag at 887 cm^{-1}.

Results and Discussion

Data Acquisition and System Capabilities. FTIR-ATR spectroscopy was utilized to monitor IB polymerization kinetics in real time. Shown in Figure 1 is the pure component spectrum of IB obtained via solvent subtraction after complete mixing and thermal equilibrium were reached. Isobutylene has a number of sharp, strong bands that may be monitored to measure its rate of disappearance. Of these bands, the strongest by a large margin is the =CH$_2$ wag, which is observed at 887 cm^{-1}. However, as this absorbance occurs below 1000 cm^{-1}, it is inaccessible to traditional FTIR-ATR monitoring via fiber optic probe technologies. The ReactIR 1000 reaction monitoring system uses a light conduit technology, which when coupled with a DiComp (diamond-composite) probe, has a low-end spectral cutoff of 650 cm^{-1}, which may be extended to 400 cm^{-1} if so desired.

The ReactIR has two different modes of reaction acquisition: standard reaction and rapid acquisition. The standard mode permits the acquisition of temperature data and the generation of multiple real time displays. Examples of such displays are the real-time waterfall plot for the decay of the 887 cm^{-1} absorbance (Figure 2) and the resulting decay profiles, using either peak height at 887 cm^{-1} or partial area under this peak (887−894.5 cm^{-1}), as shown in Figure 3.

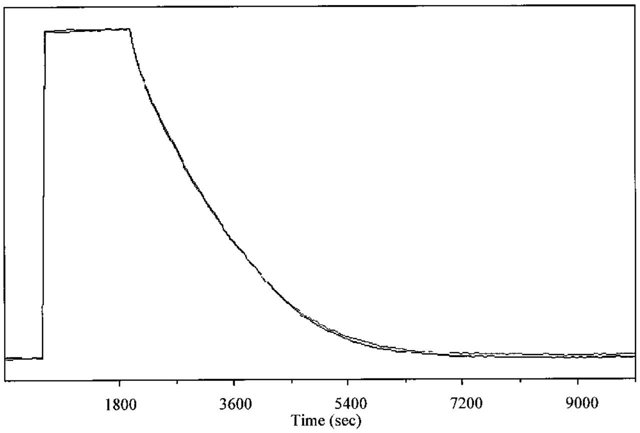

Figure 3. Real-time profiles of the =CH$_2$ wag at 887 cm^{-1}. The partial peak area and peak height have been autoscaled to show close agreement.

These real-time displays, or reaction profiles, are updated with each successive spectrum that is acquired. Their benefit is that the experimenter may make spontaneous decisions during the course of a reaction. For example, polymerization may be terminated when it has reached sufficient conversion, or the reaction sequence may be extended to permit the acquisition of additional spectra if the reaction is observed to be incomplete within the anticipated time frame. In a similar fashion, if the ReactIR were used to monitor block copolymer synthesis reactions, the time of addition of the second monomer could be directly matched with the desired extent of conversion of the primary monomer.

The ReactIR is capable of scanning at a rate of approximately 3.5 scans/s, at a spectral resolution of 8 cm^{-1}. For a reaction acquired in standard mode, the recommended minimum time period between acquisitions is 1 min, and the recommended number of scans per spectrum is 128. This number of scans requires approximately 36 s to acquire; the remaining 24 s between acquisitions is used by the instrument to reset for the next acquisition and update all real-time displays. This also provides a window of opportunity for removal of aliquots (e.g., for GPC analysis) without perturbing the system during an acquisition. For slower reactions, longer periods may be used between acquisitions, which would permit the use of a greater number of scans per spectra, thus further improving the signal/noise ratio. In fact, a longer period between data points may be required, as the ReactIR currently is limited to a total of 600 spectral acquisitions per reaction, although this limit may be increased in the future by software updates.

For faster reactions, the rapid acquisition mode may be used. Here, instrument resources are totally dedicated to data acquisition during the reaction; all profiles and displays are generated after reaction termination. At the same spectral resolution of 8 cm^{-1}, if only four scans are taken per spectra, the scan rate is approximately 2.6 scans/s, or one spectrum every 1.55 s. The experimental error is within acceptable limits (±6%), even with this few scans per spectrum. However, at this time, the experimental limitation for extremely fast reactions is not instrumentation, but rather heat transfer and mixing for the current reactor and cooling technologies. Accepting the limitations of current equipment, one may monitor reactions with half-lives on the order of 10 s. If the limitation of heat and mass transfer were overcome, reactions with half-

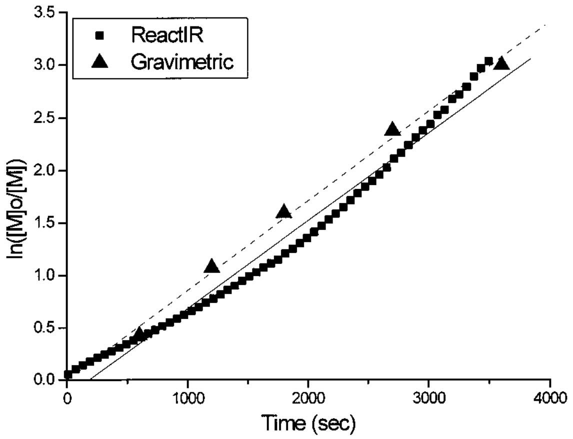

Figure 4. $\ln([M]_0/[M])$ vs time for in situ monitored polymerization and conventional gravimetric monitoring: (dashed line) linear regression of gravimetric data; (solid line) linear regression of IR data.

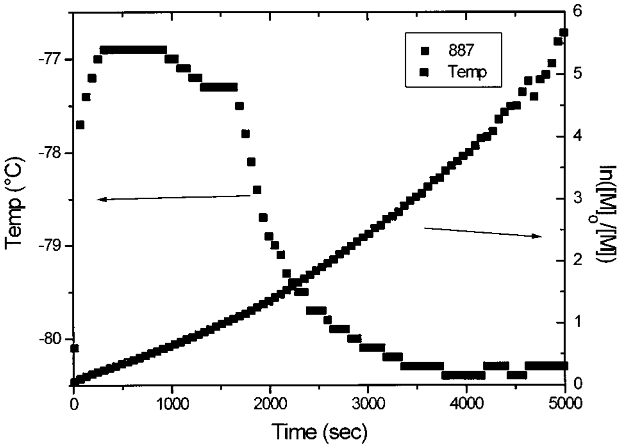

Figure 5. Reaction temperature vs time and first-order kinetic plot.

lives of less than approximately 2 s could be successfully monitored. As a final note, the rapid acquisition mode currently allows the acquisition of either spectral data or temperature data, but not both; however, this issue may be addressed in the future by the manufacturer.

Data Manipulation and Kinetic Analysis. Figure 3 shows decay profiles of the peak height at 887 cm^{-1}, as well as a partial area under this peak (887−894.5 cm^{-1}). As can be seen, the decay profiles were essentially identical. A first-order plot was constructed, assuming that the partial peak area due to the $=CH_2$ wag at 887 cm^{-1} (887−894.5 cm^{-1}) is directly proportional to IB concentration. The peak area prior to the addition of IB (solvent scan) was used as the absorbance value for [IB] = 0.0 M and, as such, was subtracted from all absorbance values to determine [IB] at any time. Figure 4 compares data generated using the current method to previously reported gravimetric yield data,[11] over the range of conversion accessible by the latter method. When the FTIR data were analyzed within this range, it yielded an apparent first-order rate constant of 8.4×10^{-4} s^{-1}, which is within 3% of the gravimetrically determined value (8.6×10^{-4} s^{-1}). However, the data acquired by FTIR are clearly nonlinear.

Inspection of the first-order plot generated from the full range of FTIR data (Figure 5) revealed a relatively high initial slope (first few data points), followed by a region of relatively constant but lower slope (150−1500 s). Thereafter, the slope smoothly rose to a second region of linearity (2300−4300 s), followed by a final minor upward curvature. The observed deviations from linearity were attributed to one major and two minor effects. The major effect causing nonlinearity up to about 3500 s (most prominently displayed in Figure 4) was a transient rise and subsequent fall in reactor temperature caused by the initial large exotherm of polymerization. The minor effects included possible changes in reaction medium polarity, caused by conversion of IB to PIB, and an artifact related to data interpretation, which is discussed below. The temperature effect was not observed in the gravimetric data because the latter are obtained from individual polymerizations conducted in culture tubes, and the much greater surface/volume ratio allows quicker dissipation of the polymerization exotherm. More importantly, however, the traditional gravimetric method cannot provide data points of sufficient accuracy and density to observe small differences in instantaneous rate. In contrast, the ReactIR has sufficient sensitivity and acquisition speed to detect such subtle changes.

The proposed temperature effect is graphically illustrated in Figure 5 by superimposing the reactor temperature profile and the first-order kinetic plot. It is readily apparent that there is a significant exotherm, one which is too large for the cooling reservoir to rapidly absorb. As such, the reaction initially warms, which retards the overall rate of reaction by decreasing the number of active ionized propagating centers. As the cooling bath overcomes the initial exotherm and the reactor begins to cool, an upward curvature is observed in the $\ln([M]_0/[M])$ graph. These initial thermal effects, so graphically illustrated by the new monitoring system, are characteristic of current batch cationic polymerization techniques. They can be minimized by the use of smaller reaction volumes, and given the sensitivity of this technique, lower initial monomer concentration may also be employed.

Figure 5 suggests two discernible regions of relative temperature stability. The first, from about 150 to 1500 s represents the dwell about the temperature maximum. Linear regression of the first-order plot within this range revealed that the data are indeed linear with $R^2 = 0.998$ and $k_{app} = 6.1 \times 10^{-4}$ s^{-1}. The second region occurred after the temperature returned to -80.0 ± 0.5 °C; here, the first-order plot was also observed to be linear ($R^2 = 0.998$ over the range 2300−4300 s), and the apparent rate constant was calculated to be 1.2×10^{-3} s^{-1}. The fact that there exist two linear regions, each associated with essentially isothermal reactor conditions, and a transition region of increasing slope and decreasing temperature, aptly demonstrates that temperature variation is the primary cause of curvature. The variation of the rate constant by a factor of 2 is reasonably consistent with the apparent energy of activation for IB polymerization (−8.5 kcal/mol) measured under these conditions using the traditional gravimetric method.[11]

Two minor effects may also have contributed to the observed deviations from expected first-order behavior. It is well documented that increasing reaction solvent polarity leads to higher rates of polymerization by shifting the equilibrium between active and dormant chain ends further toward the ionized state.[10] It is possible that conversion of IB to PIB alters the effective solvent polarity; however, the nature and extent of this effect is not well understood at this time. The second minor effect involves a small error in the $[M]_0/[M]$ values, which is significant only at high conversions and is inherent with the current method of data analysis. The error arises because the solvent baseline value prior to monomer introduction is approximately 8% higher than the asymptotic value observed at complete IB conversion. This effect is caused by dilution of solvent by PIB, and a similar error certainly exists from dilution of solvent by IB during the early stages of reaction. The use of the pure solvent baseline value as the value for $[IB] = 0.0$ M (as opposed to the value from a 1.0 M solution of PIB repeat units) causes an error in $[M]_0/[M]$ values which grows increasingly larger at extremely high conversions. The pronounced upward curvature in the first-order plot beyond 4300 s is no doubt primarily caused by this artifact, and efforts are currently being undertaken to optimize the method of data analysis to account for the dilution effect.

Aside from the early perturbations of the rate caused by less than optimal temperature control, Figure 5 shows the effective number of growing chains remains constant to at least 6.5 half-lives. It has been demonstrated that the principle chain interrupting event for IB polymerizations under these conditions is chain end rearrangement (i.e., pseudotermination), not chain transfer.[12] In line with this, GPC analysis showed the final material to have $M_n = 29\,900$ and PDI = 1.03; the former value is within 0.5% of theoretical, indicating no measurable chain transfer.

Conclusions and Future Work

Initial results generated via real-time FTIR-ATR monitoring, with light conduit and diamond-composite sensor, show this to be a powerful method for reaction monitoring and kinetic and mechanistic investigations. The high sensitivity of the method, demonstrated by accurate detection of slight rate changes caused by temperature fluctuations, is remarkable. It is encouraging that the data acquired via FTIR-ATR agrees so closely with data generated by conventional gravimetric analysis.

Current efforts are focused on further development of the method. Specifically, to eliminate any minor error caused by volume contraction during polymerization, the absorbances associated with IB will be normalized to a strong band associated with either hexane or MeCl. A very promising absorbance is the C−Cl stretch in MeCl, which is observed at 706 cm^{-1}. Additionally, efforts are also being focused to determine the effect of dilution of the solvent by IB as well as by PIB repeat units. To eliminate the difficulty of acquiring a background spectrum at the reaction temperature, a metallic sleeve will be fashioned to fit around the DiComp probe and provide metal-to-metal contact. This assembly can be equilibrated in the cold bath prior to acquisition of the background spectrum. Smaller reactors will also be utilized to maximize the surface-to-volume ratio, thus improving heat transfer. A fourth neck will also be incorporated in this reactor to facilitate the removal of aliquots, thus permitting the construction of M_n vs conversion plots to prove the absence of chain transfer. Additionally, the technique as a whole will be scrutinized and applied to numerous systems, from additional monomers to block copolymer synthesis and star-formation reactions to name a few.

In conclusion, the use of this novel method for real-time, on-line, in situ analysis holds great promise for further kinetic investigations and will enable the development of a more complete understanding of living carbocationic polymerization.

Acknowledgment. Acquisition of the ReactIR 1000 was made possible by the Defense University Research Instrumentation Program, Grant No. DAAG55-97-1-0067. Other project support was provided by the National Science Foundation through Grant No. EPS-9452857. The authors would also like to thank Joe Schwab and Dave Hobart of ASI Applied Systems (Millersville, MD) for their technical assistance and Amoco Chemicals for their donation of *tert*-butylisophthalic acid (TBIA), an initiator precursor.

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MA971293S