Articles

Real-Time Mid-IR Monitoring of the Initiation and Propagation in Epoxi-Initiated Living Isobutylene Polymerizations

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Received June 21, 1999; Revised Manuscript Received December 29, 1999

ABSTRACT: The initiation and propagation of isobutylene (IB) polymerization initiated by 1,2-epoxi-2,4,4-trimethylpentane (TMPO-1)/$TiCl_4$ was monitored by a new fiber-optic transmission mid-IR probe. The real-time IR data provided insight into the initiation mechanism. Polyether formation, isomerization of the TMPO-1 into 2,4,4-trimethylpentanal, and its complexation by $TiCl_4$ were observed, which occurred simultaneously with initiation of IB polymerization. The proposed initiating mechanism involves the formation of *tertiary* carbocations, which has been claimed to occur in the cationic polymerization of epoxides by the S_N1 mechanism. On the basis of our results, the competitive occurrence of both S_N1 and S_N2 pathways is proposed. Interestingly, ketone/$TiCl_4$ systems were found to initiate IB polymerization, albeit with very low efficiency. IR monitoring of these systems gave additional insight into the initiating mechanism. IB polymerization was monitored by following the disappearance of the second overtone of the C−H wag in the $=CH_2$ group in IB at 1780 cm^{-1} and the C=C stretch at 1655 cm^{-1}. The linearity of first-order monomer consumption plots and the production of nearly uniform polyisobutylenes (PIBs) ($M_w/M_n = 1.06-1.13$) indicated living conditions.

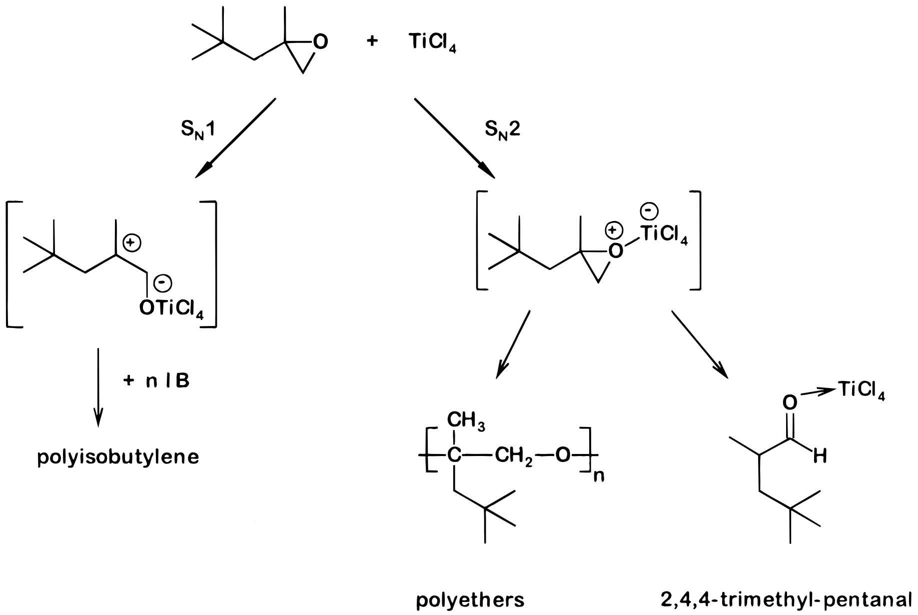
Introduction

Recently, we have discovered a new class of initiators, epoxides, for the carbocationic polymerization of isobutylene (IB).[1] Evidence was presented that selected substituted epoxides can effectively initiate living IB polymerization, and a mechanistic scheme was proposed for the initiation and propagation.[2] The proposed mechanism was based on pathways suggested for the cationic polymerization of epoxides, according to which polymerization may proceed via S_N1 or S_N2 mechanisms. The former would involve a *tertiary* carbocation intermediate, while the latter would proceed via an oxonium ion intermediate. This mechanism is still controversial and is debated.[3] We theorized that if the cleavage of a substituted epoxide would indeed occur via an S_N1 mechanism, the carbocationic polymerization of an olefin such as IB could be initiated by the *tertiary* carbocations that would form upon S_N1 cleavage of the epoxi ring by a Lewis acid such as $TiCl_4$ (see Scheme 1). Following the first initiating step, the *tertiary* carbocation would be capped by a *tert*-Cl end group, and the equilibrium between *tert*-chloride capped PIB and small amounts of active ion pairs (with both monomeric and dimeric counteranions) would be established.[4] Our hypothesis was proven by the fact that 2,4,4-trimethylpentyloxirane-1,2 (TMPO-1), 2,4,4-trimethylpentyloxirane-2,3 (TMPO-2), α-methylstyrene epoxide (MSE), and hexaepoxisqualane (HES) in conjuction with $TiCl_4$ were shown to initiate the carbocationic polymerization of IB.[2] TMPO-2, MSE, and HES initiated living carbocationic polymerization. Polyisobutylenes (PIBs) prepared by the above epoxide/$TiCl_4$ initiating systems were shown to carry *tert*-Cl end groups, in line with the proposed propagation mechanism. The proposed initiating mechanism infers that some of the initiator would be lost due to side reactions such as isomerization and polyether formation via both the S_N1 and S_N2 pathways, as shown in Schemes 1 and 2. Other side reactions such as oxo−enol tautomerism or Prins reaction could also occur. This would reduce the initiator efficiency (I_{eff}), i.e., the fraction of the initiator that would lead to carbocationic polymerization. Experimental evidence has been presented that, depending on the structure of the epoxide initiator and/or experimental conditions, I_{eff} varied between 1 and 99%.[2,5,6] The proposed initiating mechanism also infers that the polymer produced would have a headgroup carrying a *primary* hydroxyl functionality. Once proven, this would be the first example of direct hydroxyl functionalization of polyisobutylene (PIB) by controlled initiation. It can be seen that there are many unanswered questions concerning these new initiating systems. Our present research was aimed to get more insight into the mechanism of the new epoxi-initiated IB polymerizations.

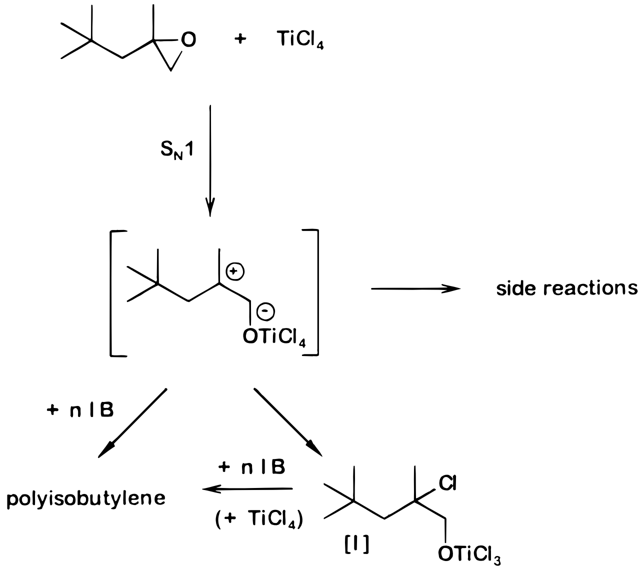
It has been shown that IR spectroscopy is eminently suitable to get insight into reaction paths.[7] Recently, we reported the first real-time fiber-optic mid-IR monitoring of living IB and styrene polymerizations using the classical living initiator 2,4,4-trimethylpentyl chloride (TMPCl).[8] The reaction was followed by an attenuated total reflectance (ATR) fiber-optic probe. This new technique is a very convenient way of monitoring both monomer consumption and polymer formation in situ in the 1000−4000 cm^{-1} range. The Storey group[9] has

10.1021/ma990983o CCC: $19.00

Scheme 1. Possible Reactions between TMPO-1 and $TiCl_4$



Scheme 2. Proposed Initiation Pathway of TMPO-1/ $TiCl_4$ Initiated IB Polymerization



also devoted considerable time and effort to a similar method using a conduit technology, which can also monitor in the fingerprint (<1000 cm^{-1}) range. Long et al. used this technique for the real-time monitoring of living radical polymerization.[10] Mid-IR real-time monitoring gives us unparalleled insight into the polymerization process, as will be demonstrated in this paper. The development of a new technique using a very sensitive fiber-optic transmission (TR) IR probe will be described. This paper will discuss the in situ real-time monitoring of the initiation and propagation of IB polymerizations initiated by 1,2-epoxi-2,4,4-trimethylpentane (TMPO-1), 2-butanone (Bu=O), and acetophenone (AcP=O) in conjunction with $TiCl_4$ by our new fiber-optic mid-IR technology in detail.

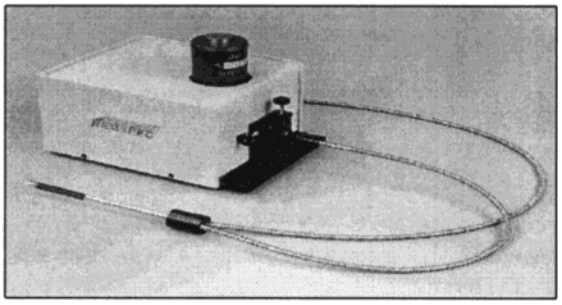
Experimental Section

Materials. a. Initiators. TMPO-1 was synthesized by reacting the corresponding olefin (2,4,4-trimethyl-1-pentene, TMP (Aldrich)) with pure 3-Cl-peroxybenzoic acid (CPBA) in dichloromethane (CH_2Cl_2, Caledon) as described.[2] TMPO-1 was further purified by vacuum distillation ($p = -100$ kPa) and the purity checked by ^{1}H NMR and RI (bp = 74−75° C, $n^{20}_D = 1.4155$). 2-Butanone (Bu=O) and acetophenone (AcP=O) (Aldrich) were distilled before use.

b. Other Materials. Methyl chloride (MeCl) and isobutylene (IB) (Matheson) were dried by passing the gases over a dryer column packed with $CaCl_2$ and BaO before condensing them from the gas phase. Hexane (Aldrich) was distilled off CaH_2. Titanium tetrachloride ($TiCl_4$), di-*tert*-butylpyridine (D*t*BP), *d*-chloroform ($CDCl_3$), calcium hydride (CaH_2), magnesium sulfate ($MgSO_4$), and dichloromethane (CH_2Cl_2) (Aldrich) were used as received.

Procedures. a. Polymerizations. Polymerizations were carried out in a Mbraun LabMaster 130 glovebox under dry nitrogen (BOC) at −80 °C. The moisture (<1 ppm) and oxygen (~5 ppm) content were monitored. The hexane bath was cooled with an FTS Flexi cool immersion cooler. A 500 mL round-bottom flask equipped with an overhead stirrer was charged with MeCl and Hx (40/60 v/v). The initiator was added to the mixture, followed by the addition of D*t*BP (concentrations are specified in the text or figure captions). Depending on the addition sequence, the reaction was started either by the addition of a chilled stock solution of $TiCl_4$ in Hx following the addition of IB or by IB following the addition of $TiCl_4$. Polymerizations were allowed to proceed until the IB had been depleted, and the reactions were terminated by the addition of prechilled methanol. PIBs were recovered by precipitation from methanol and dried in a vacuum oven. Final conversions were determined gravimetrically.

b. IR Monitoring. The liquid transmission probe (Remspec Inc.), interfaced with a Bio-Rad FTS 175C FTIR unit (source cable) and a MID-IR fiber-optic detector module (a liquid nitrogen cooled 0.5 × 0.5 mm MCT detector, receiver cable), shown in Figure 1, was fed into the drybox through a port and immersed into the reactor. For best signal output the attached cable ends were aligned manually; this could be done easily in 10−15 min. Optimum signal/noise ratios (>10) were obtained when the center burst maximum (negative peak on the on-screen display) was about −5 to −7 V at a sensitivity (amplifier gain) between 1 and 3 within the ±10 V signal range. To cool the infrared probe to the reaction temperature of −80 °C, the TR sensor was kept above the surface of the solvent mixture for 15 min, before immersing it into the cold liquid. At a resolution of 8 cm^{-1}, sufficient for IR measurements in the liquid phase, IR spectra (64 acquisitions each) were taken every 14 s and collected into one multifile (150−250 spectra) by the Bio-Rad Win-IR software. The kinetic data


Detector module with fiber optic cables

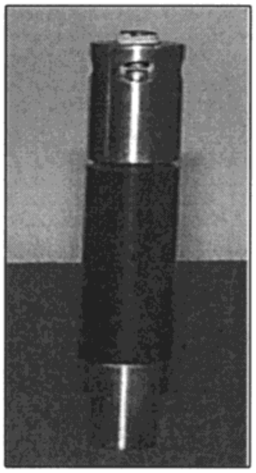

TR probe tip

Figure 1. Liquid transmission IR probe with detector.

were evaluated with the REMPAEK software package (REMSPEC Inc.) This software application for GRAMS/32 is designed to take a large set of spectral data and calculate the area of an individual peak in each spectrum. To evaluate the kinetic data, the main multifile was split into individual subfiles via the application program *mfutils* within GRAMS/32. The peak areas were calculated using the Lorentzian curve fit in REMPAEK. Monomer consumption data were obtained from the corresponding peak areas, or in the case of overlap the corresponding peak heights, which were shown to be proportional to IB concentration (see Results and Discussion).

c. Initiator and Polymer Analysis. NMR analysis was performed in deuterated chloroform ($CDCl_3$); TMS was used as an internal reference. Spectra were recorded on Varian Gemini (200 and 300 MHz) spectrometers. RI measurements were carried out with a Bausch&Lomb refractometer. Polymer molecular weights (MW) and molecular weight distributions (MWD) were determined by size exclusion chromatography (SEC) using a Waters system equipped with six Styragel-HR columns (100, 500, 10^3, 10^4, 10^5, and 10^6 Å pore sizes), thermostated at 35 °C, a Dawn DSP 18 angle laser light scattering detector (Wyatt Technology), a Waters 410 DRI detector thermostated at 40 °C, and a Waters 996 photodiode array PDA detector set at 254 nm. THF, freshly distilled from CaH_2, was employed as the mobile phase and was delivered at 1 mL/min. ASTRA (Wyatt Technology) was used to obtain absolute MW data with $dn/dc = 0.093$ for polyisobutylene (PIB) in THF.

Results and Discussion

Development of the TR Probe. The new TR probe, shown in Figure 1, was developed in close collaboration with Remspec Inc. The new ATR head consists of a 3 in. zinc selenide crystal attached to the fiber-optic cables, and is held in place by a mechanical seal housed within a plastic sleeve. The TR head is screwed directly onto this assembly. The adjustable mirror allows the use of variable path length, most suitable for the specific reaction conditions. This probe is able to monitor reactions in very dilute (mmol/L) solutions. In comparison to the original probe, the new design prevents the attached fiber-optic cable to get into direct contact with the cold (−80 °C) reaction mixture, which is the main reason for damage through freeze fracture. To avoid this latter aspect, the original probe had to be cooled slowly in a time range of several hours. The modified model allows the probe to cool in a relatively short time (<15 min) and operate at low temperatures (−80 °C) without freeze fracture, making it a very powerful technique in polymer science and engineering. The flexible fiber-optic cable allows for easy maneuverability. Alignment of the probe is very easy, and intensive signals with low signal-to-noise ratio (<10) can be obtained. This probe has been used in our lab for more than a year now. We used this convenient mid-IR technique to monitor the initiation and propagation in TMPO-1/$TiCl_4$ initiated IB polymerization. Calibration with known IB concentrations demonstrated direct proportionality between both the area and height of the 1655 cm^{-1} band (C=C stretch) in the 0.001−0.5 mol/L IB range and the 1780 cm^{-1} band (second overtone of the $CH_2=$ wag in the 0.3−6 mol/L IB range. Because of the sensitivity of the TR probe, the 1655 cm^{-1} band saturates beyond 0.5 mol/L IB concentration so the proportionality would not apply. On the other hand, the 1780 cm^{-1} band can be monitored well only above about 0.3 mol/L IB concentration. With the ATR probe, used to monitor living IB polymerizations,[4,8] the 1655 cm^{-1} peak is proportional to IB concentration up to 6 mol/L, but this probe is not sensitive enough to pick up the 1780 cm^{-1} band. With the new TR probe, both of these bands will be used to monitor the kinetics of monomer consumption.

In-Situ Real-Time IR Monitoring. According to the mechanism proposed for the initiation and propagation in epoxi/Lewis acid initiated IB polymerizations,[2] initiation necessitates the formation of a *tertiary* carbocation (see Scheme 2), which was said to proceed by an S_N1 mechanism.[3] This reaction is in competition with side reactions such as shown in Scheme 1. Carbocationic initiator efficiency (I_{eff}) will be defined by the competition between pathways of carbocationic polymerization or side reactions relative to IB polymerization. For instance, while 40% I_{eff} was reported for MSE/$TiCl_4$, for TMPO-1/$TiCl_4$, only 3% I_{eff} was found under the conditions investigated.[2] This indicates that side reactions dominated in the latter system. We set out to investigate this system by real-time in-situ IR monitoring.

The reaction pathway proposed for the polymerization, shown in Scheme 2, implies that if TMPO-1 is cleaved in the absence of IB, the S_N1 pathway would yield compound [I]. This *tert*-Cl is expected to be a good initiator. In this case more than an equimolar amount of $TiCl_4$ relative to TMPO-1 would be necessary to initiate polymerization; an equimolar amount would be tied up in the formation of [I] and the side reactions, so there would be no free $TiCl_4$ to ionize [I]. If excess $TiCl_4$ were available, following the initiation step propagation would proceed in a “classical” manner via the active/dormant equilibrium between *tert*-chloride capped chains and active ion pairs.[4] If, however, TMPO-1 would be cleaved in the presence of IB, the transition carbocation

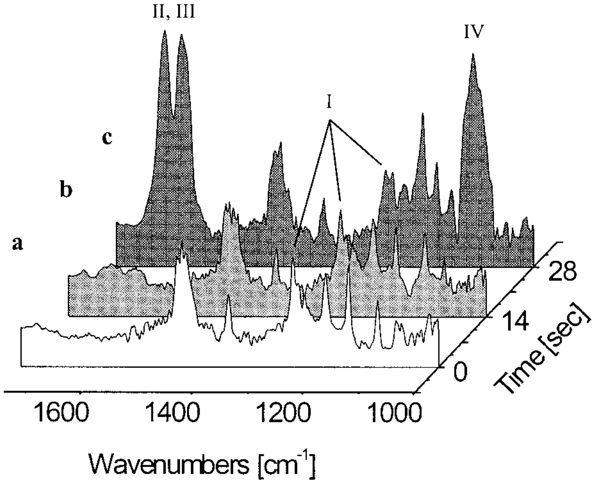


Figure 2. IR spectra of TMPO-1 before (a) and after (b, c) reaction with $TiCl_4$ in 1:1 molar ratio. [TMPO-1] = 0.1 mol/L; [$TiCl_4$] = 0.1 mol/L; Hx/MeCl 60/40; [D*t*BP] = 7 mmol/L; *T* = −80 °C.

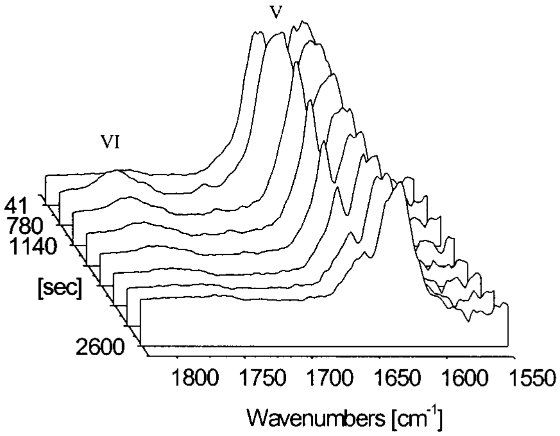


Figure 3. Real-time IR monitoring of IB polymerization: olefinic region. Addition sequence: (1) TMPO-1; (2) $TiCl_4$; (3) IB; (4) additional $TiCl_4$. [TMPO-1] = 0.1 mol/L; [$TiCl_4$] = 0.1 mol/L + 0.2 mol/L. $[IB]_0$ = 0.3 mol/L; Hx/MeCl 60/40; [D*t*BP] = 7 mmol/L; *T* = −80 °C.

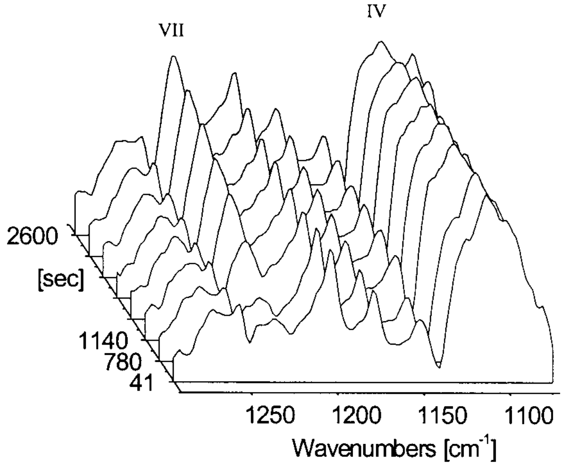


Figure 4. Real-time IR monitoring of IB polymerization: aliphatic region. Addition sequence: (1) TMPO-1; (2) $TiCl_4$; (3) IB; (4) additional $TiCl_4$. [TMPO-1] = 0.1 mol/L; [$TiCl_4$] = 0.1 mol/L + 0.2 mol/L. $[IB]_0$ = 0.3 mol/L. Hx/MeCl 60/40; [D*t*BP] = 7 mmol/L; *T* = −80 °C.

should lead to polymerization. After the first reversible end capping event, however, still excess $TiCl_4$ would be necessary for further propagation. To check these hypotheses, we investigated the cleavage of TMPO-1 by $TiCl_4$ in the absence and in the presence of IB.

Initiation: Reaction of TMPO-1 with $TiCl_4$ in the Absence of IB. TMPO-1 was mixed with an equimolar amount of $TiCl_4$ in the absence of IB, and the reaction was monitored with the new fiber-optic TR technique. Figure 2 shows the IR spectra of TMPO-1 before (a) and after reaction with $TiCl_4$ (b, c). The reaction stopped after 28 s or within two IR scan sets. Opening of the epoxide ring was demonstrated by the decreasing intensity of the band at 1260 cm^{-1} (I), characteristic of the C−O−C stretching in an epoxide ring. However, only a fraction of the epoxi rings opened, as an intensive band (I) was still present in the final spectrum (scan set c). The two signals at 1665 (II) and 1635 cm^{-1} (III), evident in scan set (b) and very strong in spectrum (c), can be assigned to 2,4,4-trimethylpentanal-1 (TMPA-1) and TMPA-1 complexed with $TiCl_4$ (TMPA-1→$TiCl_4$), respectively. The isomerization of epoxides by Lewis acids is a well-known reaction,[11,12] while complexation with $TiCl_4$ was shown to shift the carbonyl stretch of aldehydes (1765−1645 cm^{-1}) to lower wavenumbers.[13,14] The broad band at 1100 cm^{-1} (IV) that appears in spectrum (c) is typical of polyethers, forming by self-polymerization of the TMPO-1 and which is considered to be a side reaction in terms of the proposed mechanism (Scheme 2). These reactions proceeded simultaneously and none proceeded to completion, most likely due to the limited amount of $TiCl_4$ available. To monitor the initiation step, IB was added to the reaction after an initial delay of 13 min (780 s in Figure 2), and the reaction mixture was monitored over a period of 6 min. No change of intensity of the 1655 cm^{-1} peak characteristic of the C=C stretching in IB was observed (from 780 to 1140 s in Figure 3), which indicated that no species were available in the reaction mixture to initiate polymerization. Thus, if the S_N1 pathway were active during the reaction between TMPO-1 and $TiCl_4$ in the absence of IB, after the formation of the intermediate carbocation, a neutral compound such as [I] in Scheme 2 would have formed. Since no free $TiCl_4$ was available, no initiation was possible. Addition of excess $TiCl_4$ was necessary to produce *tertiary* carbocations either by the ionization of [I] or by S_N1 cleavage of the yet unopened epoxi rings and to start the polymerization of IB. Polymerization was evidenced by the depletion of IB monitored by the progressive disappearance of the characteristic peaks in the olefinic area of IB (starting at 1140 s in Figure 3): the signal at 1655 cm^{-1} (V, C=C stretch) and the second overtone of the C−H wag in the =CH_2 group in IB at 1780 cm^{-1} (VI). The progressively growing signal at 1230 cm^{-1} (VII in Figure 4) was identified as the vibrations of the distorted carbon tetrahedrons (−$C(CH_3)_2$ groups) in the forming PIB.[15]

The above results demonstrated that when 1 mol equiv of $TiCl_4$ was reacted with TMPO-1 in the absence of IB, but otherwise under polymerization conditions, only a fraction of the TMPO-1 reacted. Real-time IR monitoring evidenced the formation of both uncomplexed and complexed TMPA-1, but no polymerization was seen upon the addition of IB, and productive initiation required the addition of excess $TiCl_4$.

Initiation: Reaction of TMPO-1 with $TiCl_4$ in the Presence of IB. Figures 5 and 6 show IR spectra of a polymerization initiated by reacting TMPO-1 with excess $TiCl_4$ in the presence of IB. Immediately after

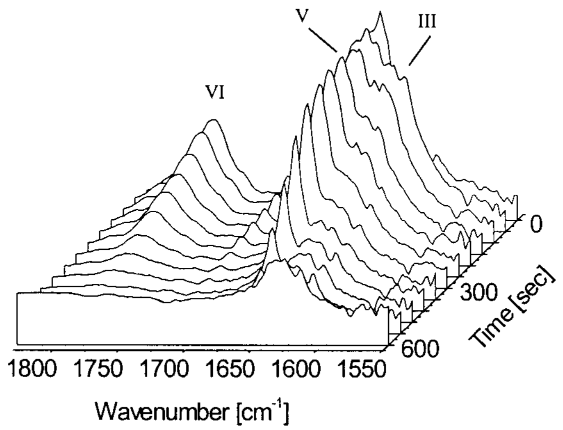


Figure 5. Real-time IR monitoring of IB polymerization: olefinic region. Addition sequence: (1) TMPO-1; (2) IB; (3) $TiCl_4$; [TMPO-1] = 0.1 mol/L; [$TiCl_4$] = 0.3 mol/L. $[IB]_0 = 1$ mol/L; Hx/MeCl 60/40; [D*t*BP] = 7 mmol/L; $T = -80$ °C.

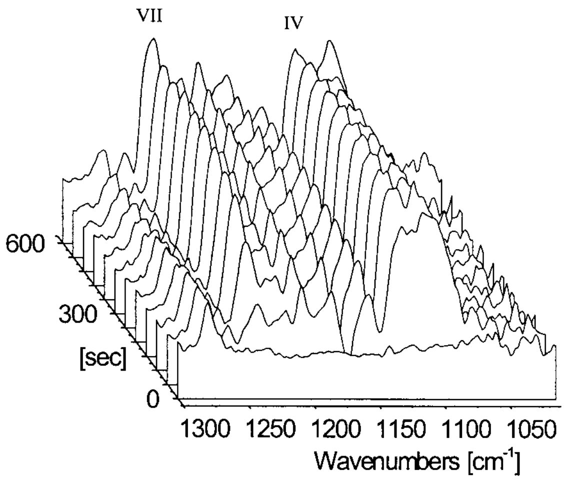


Figure 6. Real-time IR spectra of IB polymerization: aliphatic region. Addition sequence: (1) TMPO-1; (2) IB; (3) $TiCl_4$; [TMPO-1] = 0.1 mol/L; [$TiCl_4$] = 0.3 mol/L. $[IB]_0 = 1$ mol/L; Hx/MeCl 60/40; [D*t*BP] = 7 mmol/L; $T = -80$ °C.

the addition of the $TiCl_4$ into the reaction mixture containing TMPO-1 and IB with the solvents and D*t*BP, both the isomerization (TMPA-1→$TiCl_4$, shoulder II in Figure 5) and polyether formation (IV in Figure 6) could be watched in real time. Polymerization ensued immediately, as evidenced by the progressively disappearing IB signals (V and VI in Figure 5) as well as the progressively growing PIB signal (VII in Figure 6). The disappearance of the epoxi rings could not be monitored due to the interference with this 1230 cm^{-1} PIB signal.

The results presented above demonstrated that when the epoxi ring in TMPO-1 was cleaved by $TiCl_4$ in the absence of IB, the formation of polyethers, TMPA-1 and TMPA-1→$TiCl_4$, could be observed by real-time IR monitoring. Addition of IB did not result in polymerization until the addition of an excess of $TiCl_4$. In contrast, when the TMPO-1 was cleaved in the presence of IB and excess $TiCl_4$, parallel to polyether formation and isomerization, polymerization of IB ensued. Similar reactions were observed in MSE/$TiCl_4$ initiated IB polymerizations; the results will be reported separately. This strongly corroborates the initiating mechanism proposed for epoxi/$TiCl_4$ initiated IB polymerization.^{2}

IB Polymerization Initiated by Ketone/$TiCl_4$ Complexes (?). TMPO-2, an "internal" epoxide, was shown to be a slightly better initiator than TMPO-1 in conjunction with $TiCl_4$. Unfortunately, the real-time monitoring of the cleavage of the epoxi rings during polymerization could not be observed due to the interference of the 1230 cm^{-1} PIB signal with the 1260 cm^{-1} oxirane signal. The isomerization of TMPO-2 by $TiCl_4$ would lead to a ketone. This gave us the idea to investigate the reaction of ketones with $TiCl_4$ in the presence of IB. Figure 7 shows representative IR scans for the reaction of Bu=O with $TiCl_4$ in the presence of IB. The C=O stretch signal of Bu=O at 1722 cm^{-1} (II) disappeared upon the addition of $TiCl_4$, while a shoulder appeared at 1645 cm^{-1} (III) next to the C=C stretch of the IB at 1655 cm^{-1} (V). III can be assigned to the Bu=O→$TiCl_4$ complex; this is also reinforced by the appearance of two strong signals at 1190 and 1090 cm^{-1} (IV a and b in Figure 8), characteristic of the C−H wag of the CH_3 group in the Bu=O→$TiCl_4$ complex. Surprisingly, IB polymerization ensued as evidenced by the disappearance of the 1655 and 1780 cm^{-1} (V and VI in Figure 7) IB signals and the increase of the 1230 cm^{-1} PIB signal (VII in Figure 7). The AcP=O/$TiCl_4$ combination also initiated IB polymerization. Similarly to that shown for Bu=O/$TiCl_4$, the C=O stretch of AcP=O at 1685 cm^{-1} completely disappeared upon the addition of $TiCl_4$, and new signals appeared at 1600 cm^{-1} (AcP=O→$TiCl_4$ complex) and at 1180 and 1080 cm^{-1} (C−H wag in $CH_3{-}C{=}O{\rightarrow}TiCl_4$). IB polymerization was evidenced by the disappearance of the 1655 cm^{-1} band; the

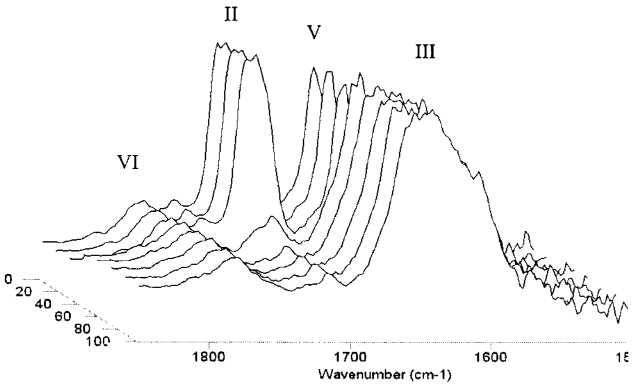


Figure 7. Real-time IR monitoring of IB polymerization: olefinic region. [2-Butanone] = 0.1 mol/L; [$TiCl_4$] = 0.4 mol/L; $[IB]_0 = 0.3$ mol/L; Hx/MeCl 60/40; [D*t*BP] = 7 mol/L; $T = -80$ °C.

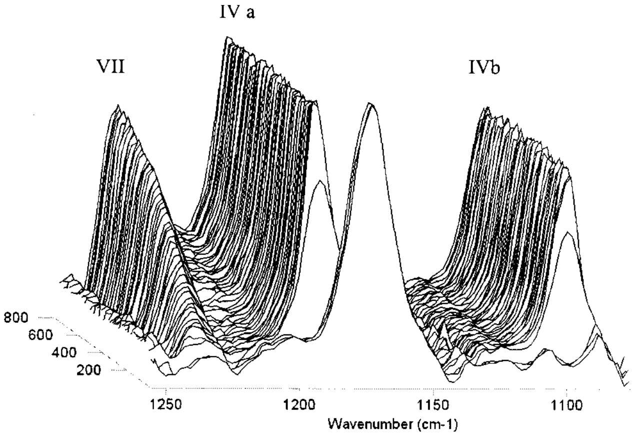


Figure 8. Real-time IR monitoring of IB polymerization: aliphatic region. [2-Butanone] = 0.1 mol/L; [$TiCl_4$] = 0.4 mol/L. $[IB]_0 = 0.3$ mol/L; Hx/MeCl 60/40; [D*t*BP] = 7 mmol/L; $T = -80$ °C.

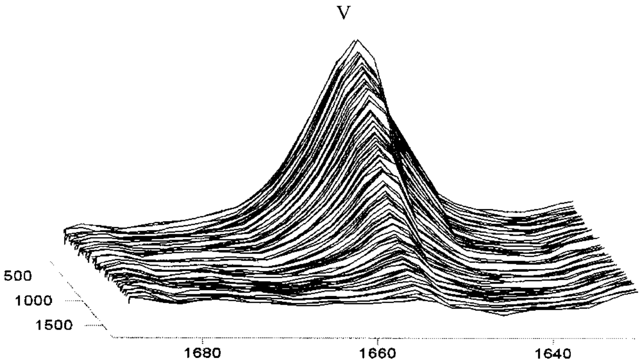


Figure 9. Real-time IR monitoring of IB polymerization: olefinic region. [Acetophenone] = 0.1 mol/L; [$TiCl_4$] = 0.4 mol/L. $[IB]_0$ = 0.3 mol/L; Hx/MeCl 60/40; [D*t*BP] = 7 mmol/L; *T* = −80 °C.

AcP=O→$TiCl_4$ signal did not overlap in this case, as shown in Figure 9.

The only way to explain the initiation of IB polymerization by ketone/$TiCl_4$ complexes is the assumption of the formation of a tertiary carbocation in a reaction shown in Scheme 3. This reaction has a low probability as demonstrated by the very low I_{eff} values. However, initiation by these ketone/$TiCl_4$ systems are undeniable as polymerization did not occur in the absence of initiators under the same conditions. While these experiments provided further insight into the mechanism of epoxide/$TiCl_4$ initiated IB polymerizations, they also raised a lot of questions. Further investigations are in progress in our laboratory.

Propagation in TMPO-1/$TiCl_4$-Initiated IB Polymerization. The progress of polymerization can be monitored by both the disappearance of the IB signals at 1780 and 1655 cm^{-1} and the appearance of the PIB signal at 1230 cm^{-1} (Figures 3−6, 8, and 9). Figure 10 shows a representative first-order plot for monomer consumption for the polymerization that was initiated by the addition of excess $TiCl_4$ to a mixture of prereacted equimolar TMPO-1/$TiCl_4$ and IB, as described in the previous section, based on peak area integration of the 1780 cm^{-1} band. Following a short induction period, the plot is linear in the detection range. The 1780 cm^{-1} peak disappeared at about 60% IB conversion. At that point, the 1655 cm^{-1} (V) peak (see Figure 3), which was saturated at the beginning of the polymerization due to the high sensitivity of the new TR probe, was in the detection range, so the IB consumption was continued to be monitored by following the disappearance of this peak. Because of the overlap of the TMPA-1→$TiCl_4$ signal with the 1655 cm^{-1} signal (see Figure 3), the peak height was used to calculate the monomer consumption plot (Figure 11). Comparison of the slopes in Figures 10 and 11 demonstrates that the monomer consumption rates are practically identical with the two methods, so both are suitable for kinetic data evaluation. The polymerization was terminated after 2600 s. A 65% conversion was achieved, and the resulting polymer had M_n = 60 000 g/mol and MWD = 1.06. The initiator efficiency was calculated to be 0.2%. The first-order monomer consumption plots for the polymerization where the TMPO-1 was cleaved in the presence of IB were also linear, but the reaction was faster with no induction period. The polymerization was terminated after 600 s. An 82% conversion was achieved, and the resulting polymer had M_n = 47 000 g/mol and MWD = 1.13. The initiator efficiency was calculated to be 1%.

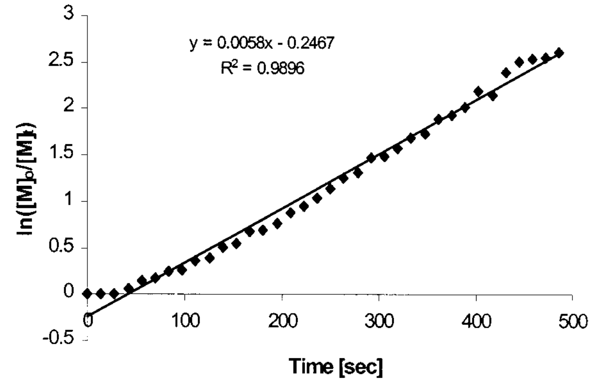
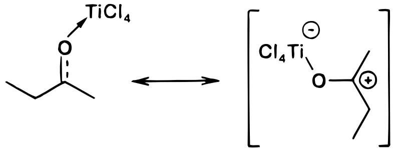


Figure 10. $\ln[M]_0/[M]_t$ versus time plot based on the 1780 cm^{-1} peak area of IB: evaluation of the spectra shown in Figure 3.

Scheme 3. Proposed Formation of *Tertiary* Carbocations in Ketone/$TiCl_4$ Initiated IB Polymerization



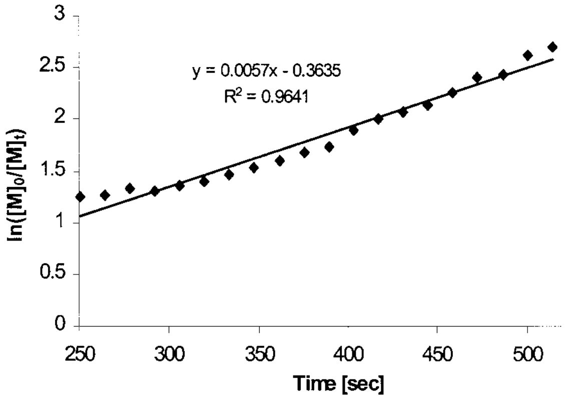
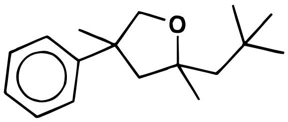


Figure 11. $\ln[M]_0/[M]_t$ versus time plot based on the 1655 cm^{-1} peak height of IB: evaluation of the spectra shown in Figure 3.

The semilogarithmic first-order plots of monomer consumption were also linear for the ketone-initiated systems. The Bu=O/$TiCl_4$ initiated polymerization was terminated at 800 s, yielding 76% conversion with M_n = 100 000 g/mol and MWD = 1.13, with 0.2% efficiency. In the AcP=O/$TiCl_4$ initiated reaction a 245 s initiation period was observed before IB polymerization started, yielding 89% conversion in 3300 s with M_n = 128 000 g/mol, MWD = 1.26, and I_{eff} = 0.2%.

Because of the high molecular weights, the structure of the polymer headgroups could not be investigated. Model experiments with diisobutylene (DIB) were unsuccessful, due to the low initiator efficiencies. Model experiments with the MSE/$TiCl_4$/DIB yielded the following compound:[16]



This, together with polymer analysis,[1,2] demonstrates controlled initiation by epoxides and direct incorporation of the oxygen group of the epoxide initiator into the polymer headgroup. Further investigations are in progress in our laboratory.

Acknowledgment. The authors acknowledge contributions by Dr. P. Melling of Remspec Inc. and financial support by the Rubber Division of Bayer Inc., NSERC and MMO of Canada. Collaboration with the Storey group via student exchange (L. B. Brister was a visiting Ph.D. student at UWO) is greatly appreciated.

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MA990983O