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New Epoxide Initiators for the Controlled Synthesis of Functionalized Polyisobutylenes

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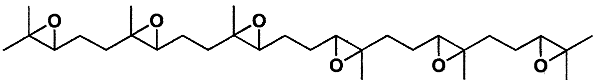
SUMMARY: The mechanism of initiation was investigated in isobutylene (IB) polymerizations initiated by epoxidized α-methylstyrene (MSE) and 1,2-epoxy-2,4,4-trimethylpentane (TMPO) in conjunction with $TiCl_4$. The proposed mechanism predicts primary OH head groups and tertiary Cl end groups in the PIB. Model studies conducted with MSE/$TiCl_4$ and diisobutylene lead to ring closure yielding a substituted furanyl structure. Real-time fiber-optic refractive index monitoring was used to follow the initiation with the TMPO/$TiCl_4$ system. It was found that the cleavage of TMPO proceeds simultaneously by S_N1 and S_N2 mechanisms as proposed. The carbocation forming by the S_N1 route is proposed to initiate the polymerization of IB, but it was shown that excess $TiCl_4$ relative to TMPO was necessary for propagation. Isomerization and polyether formation by the S_N2 pathway lead to side reactions, reducing the initiating efficiency.

Introduction

It has recently been discovered that substituted epoxides can initiate the living polymerization of isobutylene (IB) (1,2). For instance, the multifunctional initiator hexaepoxysqualene (HES)



was shown to be an effective initiator in conjunction with $TiCl_4$, yielding star-branched polyisobutylenes (PIBs) with molecular weights up to M_n = 415 000 (1,3) and PIB-polystyrene (PS) star-branched block copolymers (4). The initiation mechanism proposed (2) suggested that controlled initiation by substituted epoxides such as HES would yield hydroxy head groups and tertiary chlorine end groups.

This paper will investigate the initiation of IB polymerizations with epoxidized α-methylstyrene (MSE) and 1,2-epoxy-2,4,4-trimethylpentane (TMPO) in conjunction with $TiCl_4$. Model experiments were carried out using MSE/$TiCl_4$ and diisobutylene (DIB), a non-polymerizable monomer.

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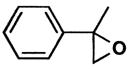
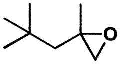


MSE



TMPO

Real-time IR monitoring of the cleavage of TMPO by $TiCl_4$ in the presence of IB provided further insight into the initiation mechanism.

Experimental

Materials

TMPO and MSE were synthesized by reacting the corresponding olefins (2,4,4-trimethylpent-1-ene, DIB, and α-methylstyrene (Aldrich) with pure 3-chloroperoxybenzoic acid (CPBA) in dichloromethane (CH_2Cl_2, Caledon) at room temperature as described (2). They were purified by vacuum distillation at 100 kPa; the purity was checked by ^1H NMR and RI (TMPO: bp = 74 –75 °C, $n^{20}_D = 1.4155$; MSE: bp = 70 °C, $n^{20}_D = 1.5214$).

Methyl chloride (MeCl) and isobutylene (IB) (Matheson) were dried by passing the gases over a drying column packed with $CaCl_2$ and BaO before condensing them from the gas phase. Hexane (Aldrich) was distilled from CaH_2. $TiCl_4$, 2,6-di-*tert*-butylpyridine (D*t*BP), $CDCl_3$, CaH_2, $MgSO_4$, and CH_2Cl_2 (Aldrich) were used as received.

Procedures

Model experiments and polymerizations were carried out in a MBraun LabMaster 130 glove box under dry nitrogen (BOC) at –80 °C. The moisture (< 1 ppm) and oxygen (~ 5 ppm) contents were monitored. The hexane bath was cooled with an FTS Flexi Cool Immersion Cooler. A 500 mL round bottom flask equipped with overhead stirrer was charged with MeCl and hexane (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 hexane following the addition of DIB or IB. The reactions were allowed to proceed for 2 h (model reactions) or until IB was depleted (polymerizations). IR monitoring was carried out using a sensitive liquid transmission fiber optic probe (Remspec Inc.), interfaced with a Bio-Rad FTS 175C FTIR unit as reported (2,5). The reactions were terminated by the addition of chilled methanol. The product of the model experiments was purified by column chromatography using silicagel, and characterized by elemental analysis and NMR. Spectra were recorded on Varian Gemini (200 and 300 MHz) spectrometers. NMR simulations were done using the Advanced Chemistry Development Inc. HNMR software. RI measurements were carried out with a Bausch & Lomb refractometer.

Results and Discussion

Model experiments

According to the proposed initiating mechanism (2), the PIBs resulting from controlled initiation by epoxides such as MSE and TMPO should have a head group carrying a primary hydroxy functionality and an end group with a tertiary Cl functionality. The incorporation of initiator into the polymer chain was demonstrated for MSE/$TiCl_4$ by triple-detection SEC and pyrolysis GC-MS analysis (1,2). The presence of tertiary Cl end groups was verified in polymers prepared with MSE, TMPO and HES by ^1H NMR spectroscopy (2). Since the initiator efficiency (I_{eff}) decreases dramatically with increasing $[I]_0/[M]_0$ ratio, it proved to be a difficult task to synthesize PIBs with low MW. Model experiments were carried out by reacting MSE with DIB, a "non-polymerizable monomer".

The reaction of epoxides and Lewis acids was proposed to follow an S_N2 pathway yielding low-molecular-weight polyethers via oxonium ions (5,6). The isomerization of epoxides by Lewis acids is also a well-known reaction; MSE was shown to isomerize into 2-phenylpropanal (PPA) very easily (7). It was also proposed that Lewis acids can cleave epoxides by S_N1 mechanism via a tertiary carbocation. The possible reactions are shown in Fig. 1.

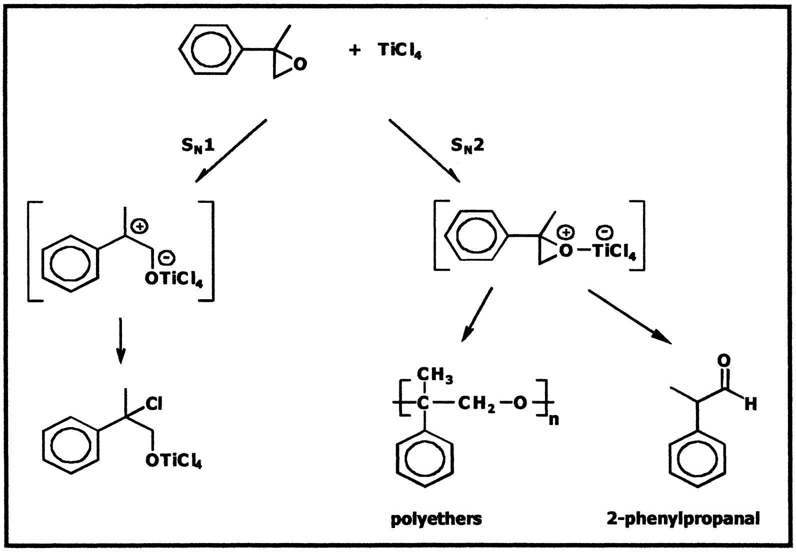


Fig. 1: Possible reactions between α-methylstyrene and $TiCl_4$

S_N1 cleavage in the presence of IB leads to polymerization, yielding PIBs with a tertiary Cl end group, since after the initiation step the equilibrium between ionic and dormant species will be established and propagation will proceed as in "conventional" living IB polymerizations (2). S_N1 cleavage in the presence of DIB, followed by termination with MeOH, as shown in Fig. 2, was expected to yield compound A or B:

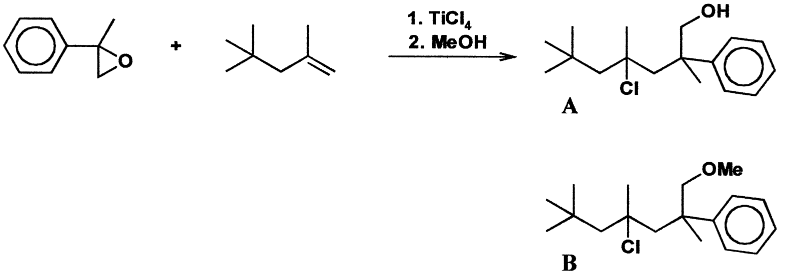


Fig. 2: Model reaction for the initiation of isobutylene polymerization with α-methylstyrene /$TiCl_4$

Figure 3 shows the NMR spectrum of the purified end product of the model experiment. The absence of a singlet methoxy signal around 3.5 ppm excluded structure B. The simulated NMR spectrum of structure A strongly resembled that of the actual spectrum shown in Fig. 3, but elemental analysis did not find chlorine in the samples. Also, IR spectroscopy revealed the absence of bands characteristic of OH groups.

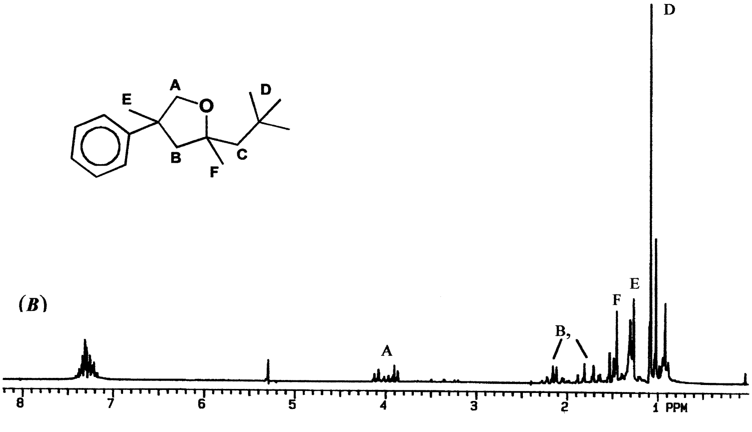


Fig. 3: ^{1}H NMR spectrum of the end product of the model reaction between α-methylstyrene/ $TiCl_4$ and diisobutylene

Figure 4 shows other possible pathways for the model reaction. The calculated composition of both compounds B and C (82.9 % C, 10.5 % H and 6.5 % O) agrees well with the results of the elemental analysis. Cumyl-type aromatic initiators were shown to be prone to indan ring formation (8), thus the formation of structure C shown in Fig. 4 would be feasible. However, IR spectroscopy showed the absence of bands characteristic of OH groups, while bands at 1180 and 1210 cm^{-1} were found, pointing to the presence of ether bonds. ^{13}C NMR revealed signals at 128.3 – 125.8 ppm, characteristic of monosubstituted phenyl groups, and signals at 75.9 – 54.5 ppm which correspond to the carbons of substituted furan rings. The simulated ^{1}H NMR spectrum of compound B agreed very well with the actual spectrum, while that of compound C was significantly different. Based on these results, the structure of the end product of the model experiment was identified as structure B in Fig. 4.

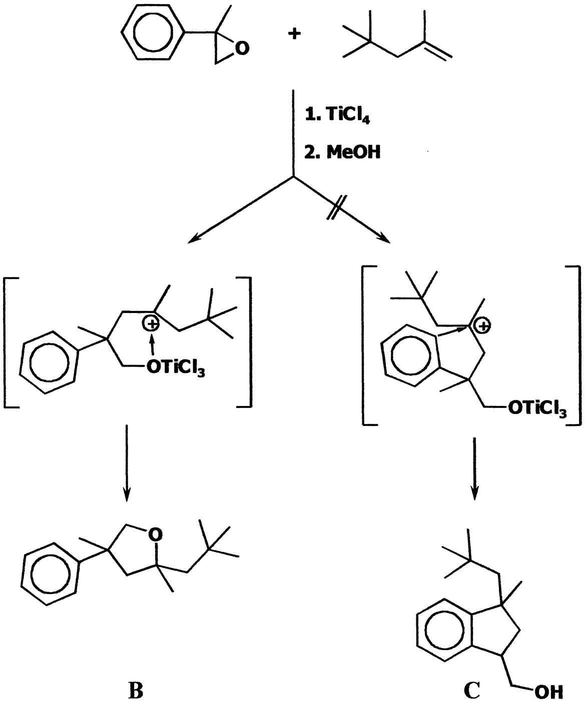


Fig. 4: Possible alternative pathways for the model reaction between α-methylstyrene/TiCl$_4$ and diisobutylene

The formation of a five-membered ring is possible under the reaction conditions of both the model experiment and polymerization. Under polymerization conditions, ring formation would reduce I$_{eff}$. However, once propagation passed the critical dimer stage, ring formation is unlikely and polymerization may proceed in the "classic" living manner. The results of the model studies prove the presence of oxygen in the head group, and infer the formation of a primary hydroxy head group in IB polymerizations initiated by epoxides such as MSE. Search for conclusive evidence for the presence of primary OH head groups is in progress in our laboratory.

In order to avoid unwanted side reactions associated with aromatic initiators, the initiation mechanism was further investigated by real-time fiber-optic mid-IR monitoring using the TMPO/$TiCl_4$ initiating system.

Initiation of isobutylene polymerization with TMPO/$TiCl_4$

Figures 5 and 6 show IR spectra of an IB polymerization initiated with TMPO/$TiCl_4$. Immediately after addition of $TiCl_4$ into the reaction mixture containing TMPO and IB with the solvents and D*t*BP, polymerization started which was evidenced by depletion of IB monitored by progressive disappearance of the signal at 1655 cm^{-1} (I, C=C stretching) and an overtone of the C-H wagging in the $=CH_2$ group in IB at 1780 cm^{-1} (II) (see Fig. 5). The progressively growing signal at 1230 cm^{-1} (V in Fig. 6) was identified as the vibrations of the distorted carbon tetrahedrons ($-C(CH_3)_2-$ groups) in the forming PIB (9). Simultaneously, both the isomerization (aldehyde formation, III and IV in Fig. 5) and polyether formation indicated by the broad band at 1100 cm^{-1} (VI in Fig. 6) could be observed in real time.

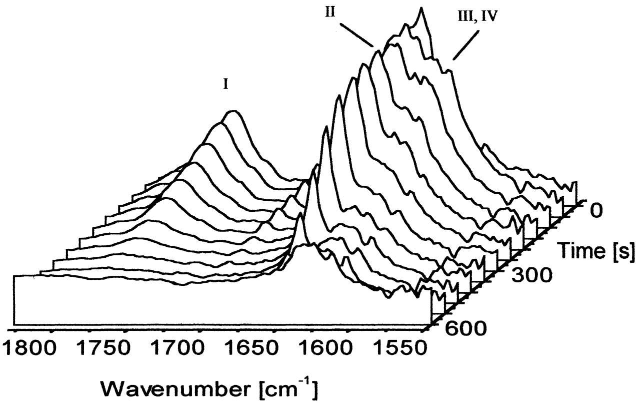


Fig. 5: Real-time IR monitoring of isobutylene polymerization ([TMPO] = 0.1 mol/L, [$TiCl_4$] = 0.3 mol/L, $[IB]_0$ = 0.3 mol/L, hexane/MeCl 60/40, [D*t*BP] = 7 mmol/L)

Under the reaction conditions, the polyether signals overlapped with the C = C stretch signal and the disappearance of the epoxide rings could not be monitored due to interference (V in

Fig. 6) with the 1260 cm^{-1} band, characteristic of the C-O-C stretching in an epoxide ring (VII).

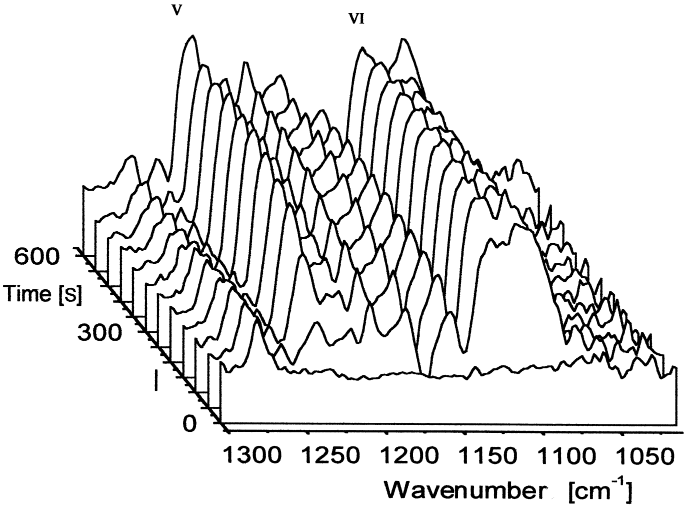


Fig. 6: Real-time IR monitoring of isobutylene polymerization (for conditions, see Fig. 5)

Therefore, TMPO was mixed with an equimolar amount of $TiCl_4$ in the absence of IB.

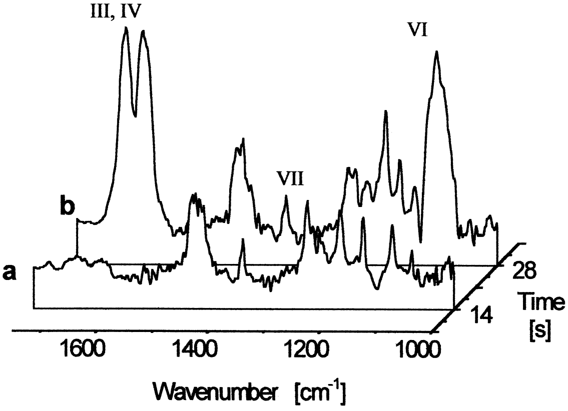


Fig. 7: IR spectra of TMPO before (a) and after (b) reaction with $TiCl_4$ ([TMPO] = 0.1 mol/L, [$TiCl_4$] = 0.1 mol/L, hexane/MeCl 60/40, [D*t*BP] = 7 mmol/L; -80 °C)

Figure 7 shows the IR spectra of TMPO after reaction with $TiCl_4$. Opening of the epoxide ring was demonstrated by the decreasing intensity of the band at 1260 cm^{-1} (VII). However, only a fraction of the epoxide rings opened, as an intensive band was still present in the final spectrum (b). The two signals at 1665 (III) and 1635 cm^{-1} (IV), evident in the scan set (a) and very strong in spectrum (b), can be assigned to 2,4,4-trimethylpentanal and that complexed with $TiCl_4$ (R-CH=O-$TiCl_4$), respectively. The isomerization of epoxides by Lewis acids is well known (7,8), and complexation was shown to shift the carbonyl band to lower wavenumbers (9,10). The polyether band at 1100 cm^{-1} (VI) that appears in spectrum (b) points to self-polymerization of the TMPO via oxonium ions (see the S_N2 pathway in Scheme 1). Upon addition of IB, no polymerization was observed by IR until excess $TiCl_4$ was added to the system. At that point, IB polymerization ensued, as evidenced by the disappearance of the olefinic peaks and the appearance of the polymer peak.

The results of the real-time IR monitoring presented here strongly corroborate the proposed initiation mechanism for epoxide/Lewis acid-initiated IB polymerization. Further characterization of the process and products is in progress.

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