Living Carbocationic Polymerization of Isobutylene by *tert*-Amyl Alcohol/BCl_3/1-Methyl-2-pyrrolidinone Initiating System

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SYNOPSIS

1-Methyl-2-pyrrolidinone has been investigated, for the first time, as an efficient electron-pair donor in conjunction with *tert*-amyl alcohol and BCl_3 in CH_2Cl_2 diluent at −40°C for the living polymerization of isobutylene. The use of this new *mono*functional *ini*tiator-trans*fer* (*minifer*) system has led to the synthesis of low molecular weight, living (near-monodisperse) polyisobutylenes carrying "ethyl" head group and "*tert*-chloro" end group (asymmetric telechelic polyisobutylenes). The nature of these groups was confirmed by ^{1}H-NMR spectroscopy. The living nature of the α-ethyl-ω-(*tert*-chloro)polyisobutylenes has been demonstrated by a linear plot, passing through the origin, of number-average molecular weight ($\bar{M}_n$) vs. the amount of polymer formed (W_p) and a horizontal N (number of polyisobutylene molecules) vs. W_p plot. These results are further substantiated by gel permeation chromatography data of these polymers, and the molecular weight distributions of these polymers are narrow (low $\bar{M}_w/\bar{M}_n$ = 1.1–1.2). The initiating efficiencies (I_{eff}) are close to 100% with this system. Dehydrochlorination of the prepolymer has yielded an isopropylidene (*exo*-olefin) end group. Structure of the end group in the resulting polymer, α-ethyl-ω-(isopropenyl)polyisobutylene, was confirmed by FTIR spectroscopy.

INTRODUCTION

Living polymerization, which proceeds in the absence of *termination* and *chain transfer,* is one of the best means to control the molecular weight and molecular weight distribution (MWD) of polymers and is of great scientific and commercial interest.[1] Since the discovery of the living anionic polymerization,[2,3] which led to several modern industrial processes,[4,5] successful attempts have been made to find conditions under which living carbocationic polymerization of olefin monomers could be achieved.[6,7]

A conventional nonliving carbocationic polymerization can be rendered living by the use of a proper electron-pair donor (ED) that eliminates undesirable side reactions such as uncontrolled initiation by protic impurities, chain transfer, and irreversible chain termination. This concept has been substantially investigated by Hagashimura et al. for vinyl ethers[8] and by Kennedy et al. for isobutylene[9] polymerizations using the classical *inifer* method.[10] According to these investigators,[9,11] the presence of an ED in these polymerizations apparently stabilizes and reduces the high intrinsic reactivity of unstable growing polymerization-active carbocations and yields polymers with narrow MWD.

In view of the recent significant advances in living carbocationic polymerizations, especially with the use of EDs such as dimethyl acetamide (DMA) and dimethylsulfoxide (DMSO) by Kennedy et al. for isobutylene,[9] we have investigated the potential use of another ED, 1-methyl-2-pyrrolidinone, for the synthesis of well-defined polyisobutylenes end-capped with *tert*-chloro groups. The great advantage of narrow MWD and well-defined telechelic polyisobutylenes is that the end group can be modified into unique, new, near-monodisperse network ionomers.[12]

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Table I Polymerization of Isobutylene (IB) by the *tert*-Amyl Alcohol/BCl_3/1-Methyl-2-pyrrolidinone System Using Incremental Monomer Addition (IMA) Technique

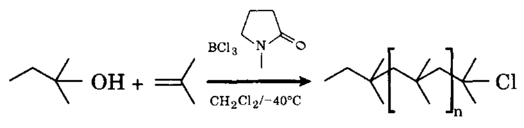
Sample No.	Time (min)	W_p (g)	$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[b]	I_{eff} (%)
1	30	0.37	1095	1.18	94
2	60	0.92	2790	1.15	93
3	90	1.69	4790	1.11	93
4	120	1.98	5810	1.09	96
5	10	0.99	NA	3.98	NA

[*tert*-Amyl alcohol] = 0.3575 mmol; [IB] = 13.35 mmol; [BCl_3] = 4.48 mmol; [1-methyl-2-pyrrolidinone] = 0.5362 mmol; CH_2Cl_2 = 20 mL; 30 min; −40°C. Samples 1–4 by IMA method. NA = not available.

[a] $\bar{M}_n$ obtained by VPO measurements.

[b] $\bar{M}_w/\bar{M}_n$ obtained by GPC measurements.

In this paper, we report the use of 1-methyl-2-pyrrolidinone as an efficient ED in conjunction with a *tert*-amyl alcohol/BCl_3 initiating system for the convenient synthesis of low molecular weight (liquid), living α-ethyl-ω-(*tert*-chloro)polyisobutylenes by ED-stabilized living carbocationic polymerization of isobutylene at −40°C as shown in Scheme 1. We also present spectroscopic evidence to prove the end functionality by ^{1}H-NMR spectroscopy.



Scheme 1

EXPERIMENTAL

Materials

tert-Amyl alcohol (Aldrich) was distilled before use. Isobutylene (IB, Aldrich) was used by condensing it under a dry nitrogen atmosphere. Methylene chloride was distilled over CaH_2 before use. Boron trichloride, anhydrous 1-methyl-2-pyrrolidinone (M-pyrol), lithium aluminum hydride (LAH), and potassium *tert*-butoxide, methanol, and hexane (all Aldrich) were used as received. Tetrahydrofuran (THF) was distilled over LAH and toluene was distilled before use.

Procedures

Polymerizations were carried out at −40°C in a low-temperature bath using dry culture tubes equipped with mechanical stirrers and screw caps. Both the *incremental monomer addition* (IMA) and *all monomer in* (AMI) techniques were used.[7] (Polymerization conditions are given in the table and figure captions). Charges were quenched with prechilled methanol. The solvents were evaporated, and the polymer was dissolved in hexane, washed with distilled water until neutral, dried over Na_2SO_4, and

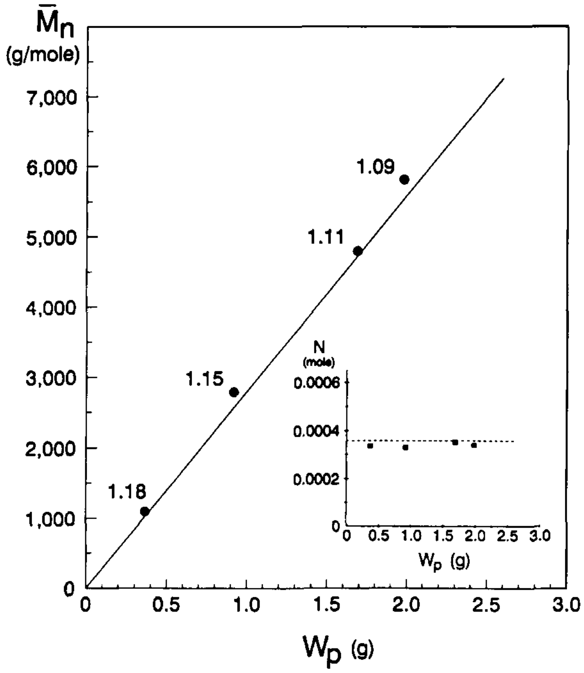


Figure 1 $\bar{M}_n$ and N, the number of polyisobutylene chains (insert), vs. the weight of the polymer (W_p) formed by *tert*-amyl alcohol/IB/BCl_3/1-methyl-2-pyrrolidinone system at −40°C by the incremental monomer addition technique (IMA): [*tert*-amyl alcohol] = 0.3575 mmol; [IB] = 13.35 mmol; [BCl_3] = 4.48 mmol; [1-methyl-2-pyrrolidinone] = 0.5362 mmol; CH_2Cl_2 = 20 mL; 30 min. Solid and dotted lines represent theoretical values. Numbers indicate $\bar{M}_w/\bar{M}_n$ values.

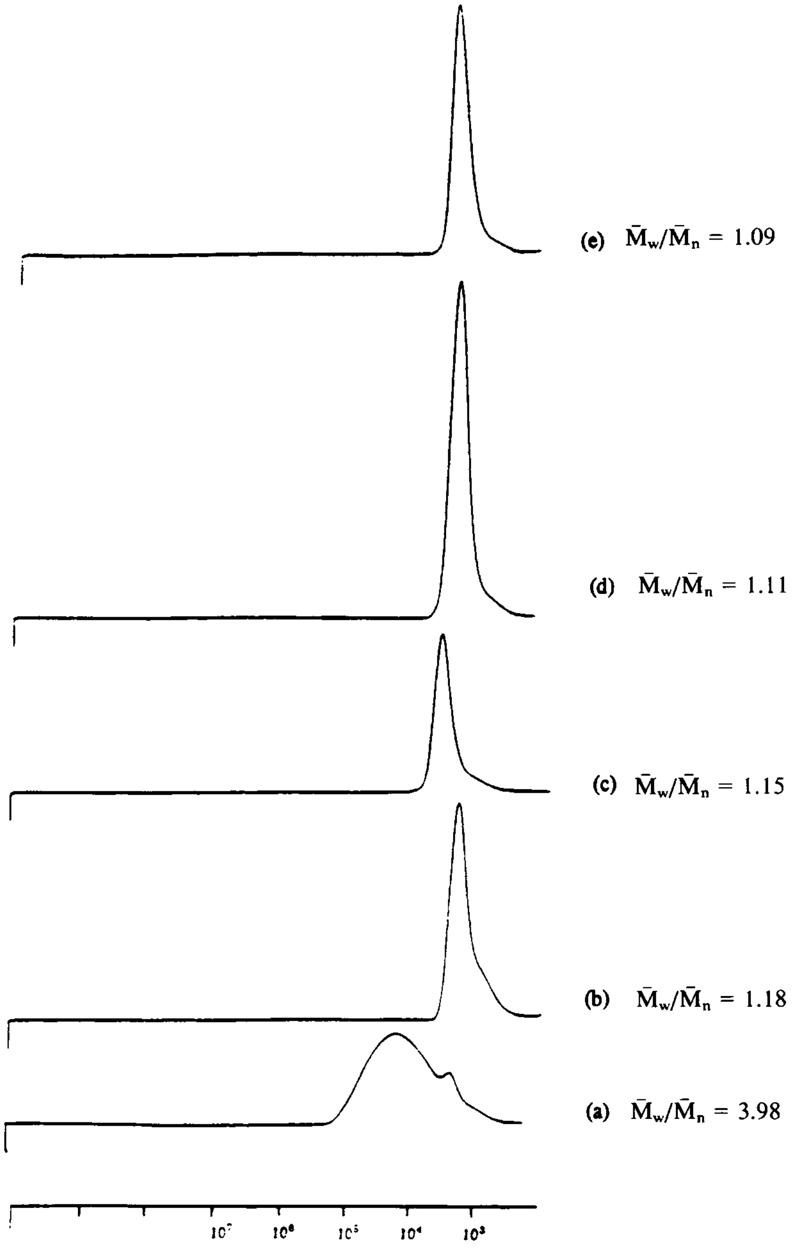


Figure 2 GPC (RI) traces of polyisobutylenes prepared by the *tert*-amyl alcohol/IB/BCl_3/CH_2Cl_2 system: (a) in the absence of M-pyrol by all monomer in (AMI) technique and (b–e) in the presence of 1-methyl-2-pyrrolidinone using incremental monomer addition (IMA) technique (reaction conditions as listed in Fig. 1).

filtered. The polymer was recovered by evaporating the solvent by rotavap and dried *in vacuo*.

The infrared spectrum was recorded on a Perkin-Elmer Fourier transform infrared spectrometer (Model 1710). ^{1}H-NMR spectrum was taken by a JEOL 400 MHz spectrometer using $CDCl_3$ solution and TMS standard.

MWDs of these polymers were determined by gel permeation chromatography (GPC) using a Waters liquid chromatograph (Model 264) provided with a separation system consisting of three columns in series and packed with Lichrogel PS400, PS40, and PS1 (E. Merck, Darmstadt, Germany) with a particle size of 10 μm. The speed of the chart recorder was 0.5 cm/min. Tetrahydrofuran (THF) was used as the mobile phase with a flow rate of 0.5 mL/min. A differential refractometer (Waters, Model 401) was used for detection and interfaced with a gas chromatograph integrator (HP 3396A) for recording. Samples of 1% solutions in THF (50 μL) were injected into the columns following filtration through a 5.0 μm filter. The data of polydispersities ($\bar{M}_w/\bar{M}_n$) were computed according to the ASTM D-3593 procedure by the GPC program developed in our laboratory. The number-average molecular weights ($\bar{M}_n$) of the polymers were determined in toluene using a Wescan Instruments vapor pressure osmometer (Model 232A) calibrated with sucrose octaacetate.

RESULTS AND DISCUSSION

Previous investigations by Kennedy et al. have shown that both DMA and DMSO are efficient EDs in conjunction with either aliphatic or aromatic *tert*-alcohols and BCl_3 or $TiCl_4$ for the living polymerization of IB.[9] We chose *tert*-amyl alcohol as an initiator for IB polymerization as there has been no report in the literature concerning its application for this purpose. The selection of M-pyrol as an ED, on the other hand, is based on its polarity index (6.7) as well as its dielectric constant (32). The values of these two parameters are close to those of the other efficient EDs, DMA (6.5 and 37.78 are the polarity index and dielectric constant, respectively), and DMSO (7.2 and 46.68).[13]

Only an insignificant amount of the polymer was formed most likely because of the protic impurities, when the monomer was mixed with BCl_3 in CH_2Cl_2. Instantaneous polymerization was observed when *tert*-amyl alcohol was used in conjunction with BCl_3. Initiation occurs in a tricomponent system, organic tertiary alcohol/BCl_3/IB, regardless of the introduction sequence of the reagents. These observations are in agreement with the earlier results of Kennedy et al.[7]

Control experiments, in the presence of either M-

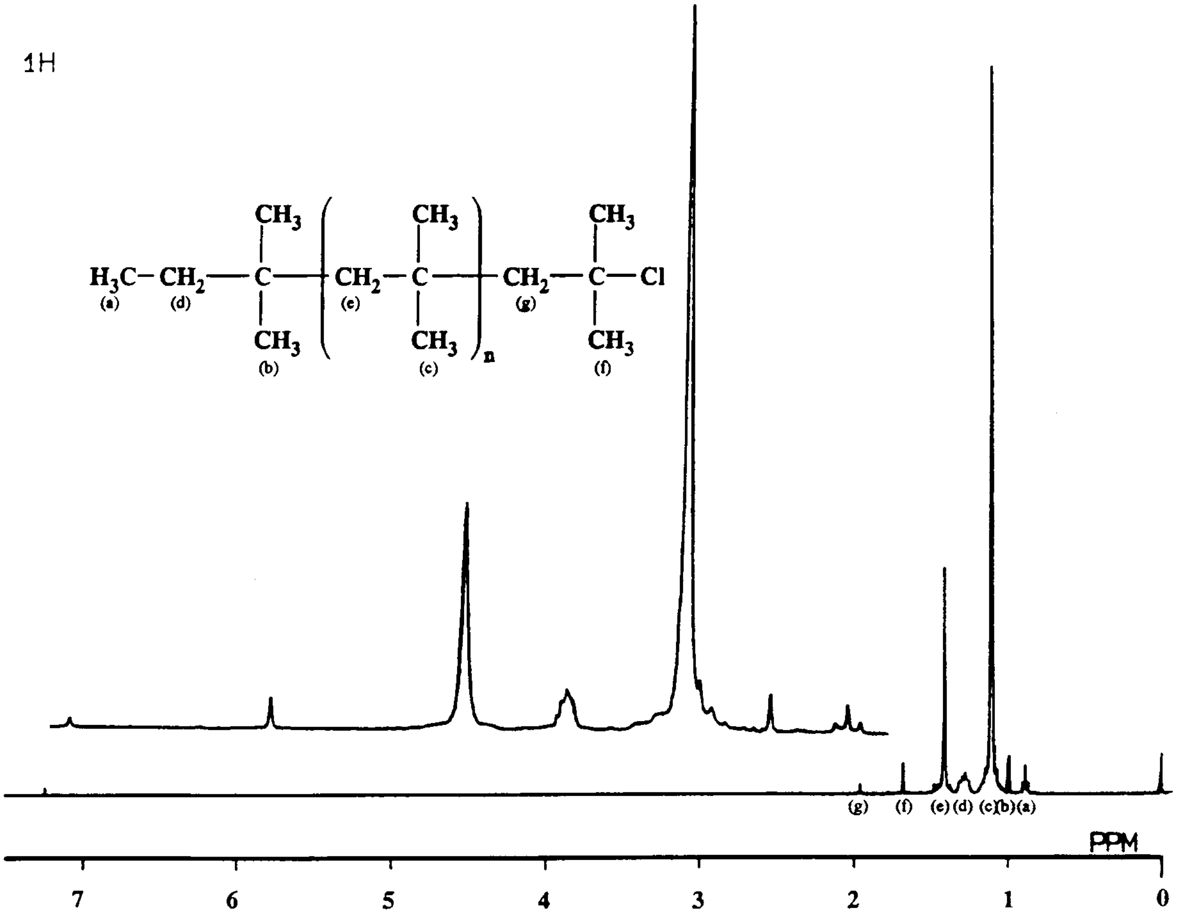


Figure 3 ^{1}H-NMR spectrum of polyisobuylene, (sample 1, see Table 1 for experimental conditions) prepared by the *tert*-amyl alcohol/IB/BCl_3/1-methyl-2-pyrrolidinone system in CH_2Cl_2.

pyrol or *tert*-alcohol alone (in the absence of BCl_3 coinitiator), indicated no sign of polymerization of IB. Polymerization was commenced by the injection of monomer after 10 min of premixing the initiator with BCl_3 in CH_2Cl_2. However, polymerization in the presence of M-pyrol was slower by cationic polymerization standard (see Table 1 for polymerization time), indicating that M-pyrol effectively modulates the reactivity of active carbocations. The conditions and results of IB polymerization initiated with *tert*-amyl alcohol/BCl_3 in the presence of M-pyrol in CH_2Cl_2 at $-40°C$ are listed in Table 1.

The diagnostic proof for the living nature of these polymers using this system has been furnished by plots shown in Figure 1. The values of $\bar{M}_n$ increase linearly with W_p (weight of the polymer formed), whereas the plot of N (number of polyisobutylene molecules formed, obtained from $g/\bar{M}_n$) vs. W_p is horizontal. Initiator efficiencies (I_{eff}) with this system are close to 100%. Further evidence for the living polymerization has been provided by the GPC studies. The GPC traces of the samples prepared by the IMA technique are shown in Figure 2. The decrease in MWD values and increase in molecular weight of the resulting polymers with increasing monomer addition in the presence of M-pyrol explicitly suggest the living nature of these polymers by the diagnostic IMA technique. The MWD of the polymer, prepared in the absence of M-pyrol, on the other hand, is wider due to the protic initiation. Thus, the addition of M-pyrol not only eliminated the side reactions triggered by the presence of protic impurities, but also showed a very significant narrowing effect on MWD of the resulting polymers.

The mechanism of initiation of this polymerization is analogous to that proposed for any *tert*-alcohol/BCl_3/DMA or DMSO-initiated IB polymerizations.[14] The addition of BCl_3 to *tert*-amyl al-

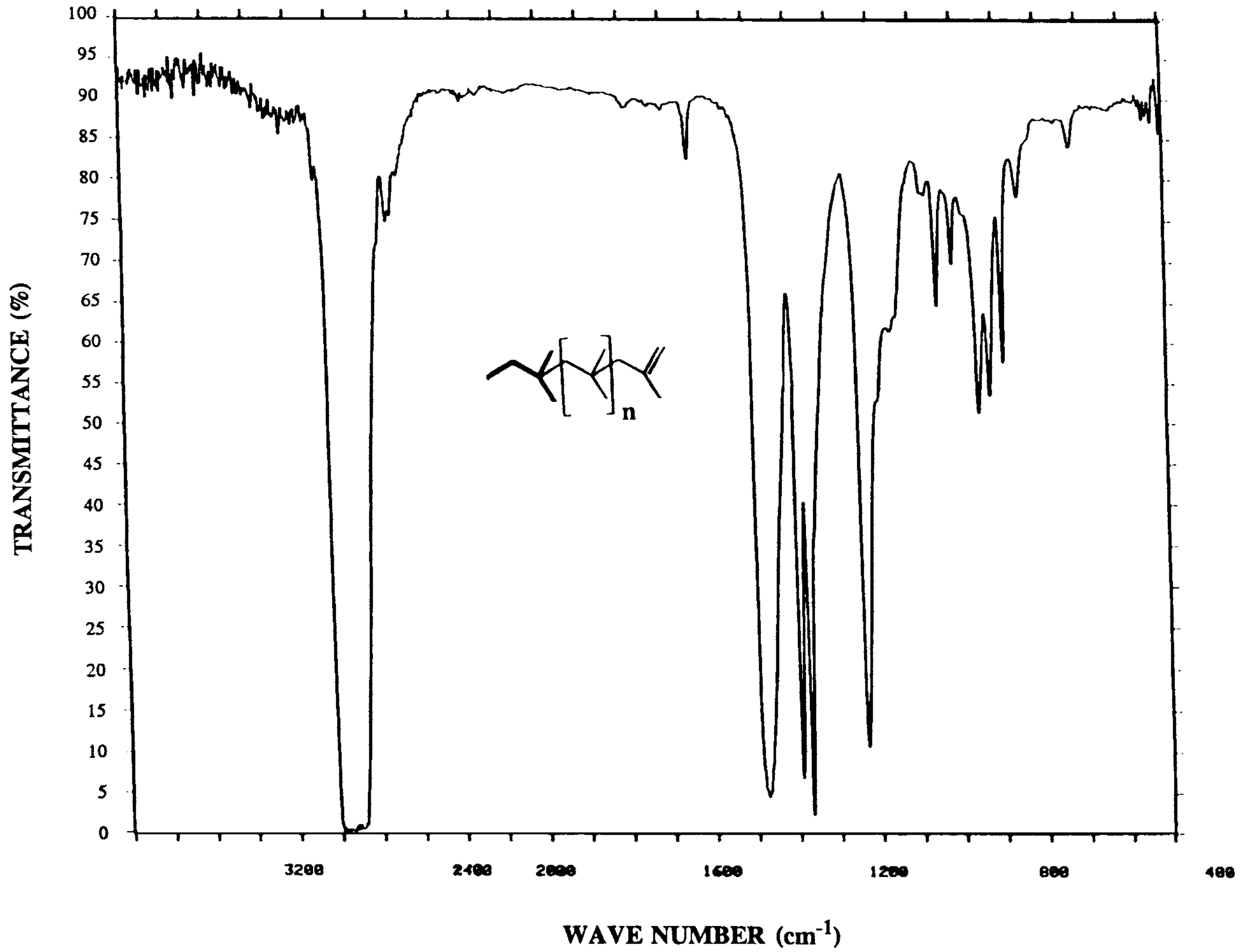
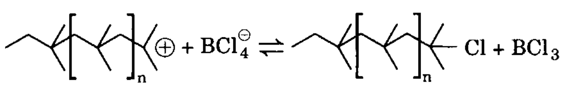


Figure 4 FTIR spectrum of α-ethyl-ω-(isopropylene)polyisobutylene obtained by the dehydrochlorination of polyisobutylene (sample 1 in Table 1) with potassium *tert*-butoxide in dry THF.

cohol initially transforms it into the corresponding chloride. The excess BCl_3, used in these polymerizations, apparently ionizes *tert*-amyl chloride. Similar to Kennedy et al.'s earlier conclusions,[14] the end-capping of these polymers by *tert*-chloro groups is visualized to involve reversible termination, as shown below:



Strong evidence for the absence of chain transfer in this type of polymerization has been furnished by the ^{1}H-NMR spectroscopic study of a representative polymer (first sample of IMA method), prepared by this *minifer* system, as shown in Figure 3. No signals corresponding to the olefinic carbons in the 3.5–5.5 δ region (which could have appeared if there had been any chain transfer during the polymerization) were detected. The appearance of the signal at 1.89 δ corresponds to the methylene protons, adjacent to the tertiary-carbon bonded to the chloro group ($-\underline{CH_2}-C(CH_3)_2Cl$). A fine triplet at 0.89 δ and a distorted quartet at 1.2 δ correspond to CH_3-CH_2-, respectively. Thus, the nature of the head and end groups are an "ethyl" and a "*tert*-chloro," respectively.

The end group functionality was also indirectly determined by the dehydrochlorination of the prepolymer (first sample in Table 1 by the IMA method) with potassium *tert*-butoxide[15] and the resulting polymer was characterized by FTIR spectroscopy. It shows the weak asymmetric stretching at 3070 cm^{-1}, symmetric stretching at 1641 cm^{-1} together with a strong doublet at 1049 and 1011 cm^{-1} and 851 cm^{-1} due to the out-of-plane bending vibrations corresponding to the characteristic olefinic absorptions of the resulting dehydrochlorinated polymer, α-ethyl-ω-(isopropenyl)polyisobutylene, as shown in Figure 4. It also shows the absorptions characteristic of $\nu C-H$ (aliphatic asymmetric and symmetric stretching vibrations) in the range of 2850–2985 cm^{-1}, $\delta C-H$ (scissoring of $-CH_2-$ and asymmetric swinging of $-CH_3$) at 1465, two peaks at 1365 and 1385 cm^{-1} corresponding to the bending of twin $-CH_3$, together with a broad band at 1224 cm^{-1} (out-of-plane bending of $-CH_2-$) conforming to the repeating units ($-CH_2-C(CH_3)_2-$) in polyisobutylenes.

According to these data, 1-methyl-2-pyrrolidinone is an efficient ED when used in conjunction with *tert*-amyl alcohol and BCl_3 for the living polymerization of isobutylene at $-40°C$ and produces α-ethyl-ω-(*tert*-chloro)polyisobutylene of narrow MWD.

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