Use of 1-Methyl-2-pyrrolidinone in Isobutylene Polymerization Initiated with 1,4-Dicumyl Alcohol/BCl_3 System, Leading to Living α,ω-Di(*tert*-chloro)polyisobutylenes

INTRODUCTION

There have been a great number of reports, especially recently, concerning the use of external electron-pair donors (EDs) in isobutylene[1-5] and vinyl ether[6-8] polymerizations, because of their beneficial effects. The use of cumyl-based initiators (esters, ethers, chlorides, alcohols) often results in cycloalkylation, leading to undesirable cyclic structures, such as indanyl and diindane in isobutylene polymerization, hampering the synthesis of perfect telechelics.[9-11] Of the several methods, developed by Kennedy et al.[1,2,10] and others,[11] the use of a deliberately added select ED in conjunction with cumyl-type initiators is the best means for the preparation of potential α,ω-difunctional polyisobutylenes,[12] because it not only prevents cycloalkylation, but also mediates controlled initiation leading to the living polymerization. A wide variety of such EDs has been successfully explored.[1-5,13] In our continuing search for new EDs, we have investigated the potential use of 1-methyl-2-pyrrolidinone as an ED for isobutylene polymerization.[13]

This article deals with the use of 1-methyl-2-pyrrolidinone as an efficient ED in conjunction with 1,4-dicumyl alcohol/BCl_3/CH_2Cl_2/−65°C initiating system for the isobutylene polymerization, resulting in the synthesis of linear living α,ω-di(*tert*-chloro)polyisobutylenes. Also provided are the experimental evidences for the elimination of cycloalkylation by FTIR, and for the controlled initiation, resulting in the living polymers by GPC studies.

EXPERIMENTAL

1,4-Dicumyl alcohol, obtained through the courtesy of the Goodyear Tire and Rubber Co., was recrystallized from methanol. All other chemicals (Aldrich), otherwise mentioned, were used as received.

Polymerizations were carried out in 75 mL culture tubes fitted with mechanical stirrers using both the *incremental monomer addition* (IMA) and *all-monomer-in* (AMI) techniques.[14] Specific conditions of polymerizations, and the concentration data, are given in Table I. Except in Run 1, the introduction sequence of the chemicals in these polymerizations was: initiator, ED, CH_2Cl_2, BCl_3, and isobutylene. The polymerizations were quenched with the addition of prechilled methanol.

Analyses of the polymers were done using a Perkin-Elmer FTIR Spectrometer (Model 1710). Molecular weights and polydispersities of these polymers were determined by a Waters High Pressure GPC (Model 264), equipped with a differential refractometer (Model 401) for detection, and interfaced with a GC integrator (HP 3396A) for recording. The calibration curve was made with polystyrene standards using degassed THF. Number average molecular weights (M_n) of the polymers were determined in toluene using a Wescan Instruments VPO (Model 232A), calibrated with sucrose octaacetate.

RESULTS AND DISCUSSION

We have considered the 1,4-dicumyl alcohol/BCl_3/CH_2Cl_2/−65°C initiating system in this work since 1,4-dicumyl alcohol, under these experimental conditions, is notorious for cycloalkylation, which hampers the clean synthesis of perfect telechelics as shown below.

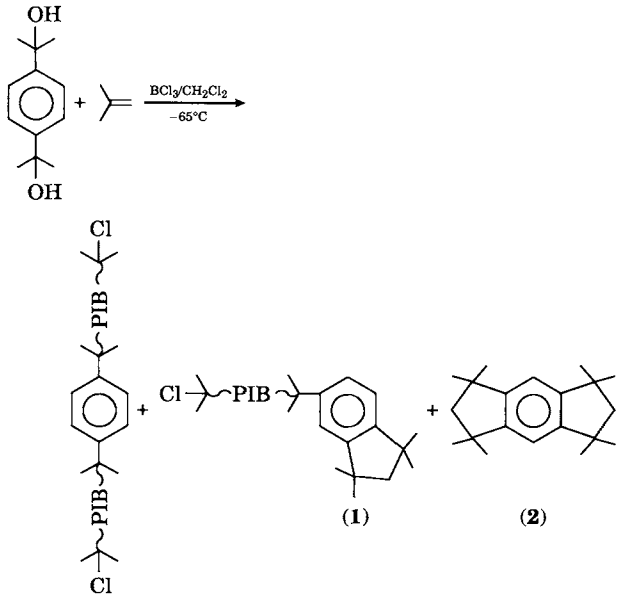

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Table I Polymerization of Isobutylene

Run No.	ED	Time (min)	W_p (g)	M_n[a]	M_w/M_n	I_{eff}	Remarks
1	None	20	0.81	NA[b]	4.12	NA[b]	Cyclic side products[c]
2	M-Pyrol	20	0.451	1480	1.18	98.6	Telechelic[c]
3	M-Pyrol	20	0.74	2470	1.24	96.9	Telechelic[c]

[IB] = 12.288 mmol; [1,4-Dicumyl alcohol] = 0.309 mmol; [BCl_3] = 3.708 mmol; [1-Methyl-2-pyrrolidinone] or M-pyrol = 0.618 mmol; CH_2Cl_2 = 15 mL; Temp = −65°C; Addition of IB after 10 min of premixing the initiator/M-pyrol with BCl_3; 1 and 2 by AMI method, and 3 by IMA method.

[a] VPO measurements.

[b] NA = not available.

[c] FTIR analysis.

To prevent cycloalkylation, we have employed a cyclic ED, 1-methyl-2-pyrrolidinone. In the absence of the ED, instantaneous polymerization occurred, resulting in a high molecular weight polymer of high polydispersity (broad MWD), indanyl (**1**), and diindane (**2**) as a result of uncontrolled initiation. On the other hand, the use of 1-

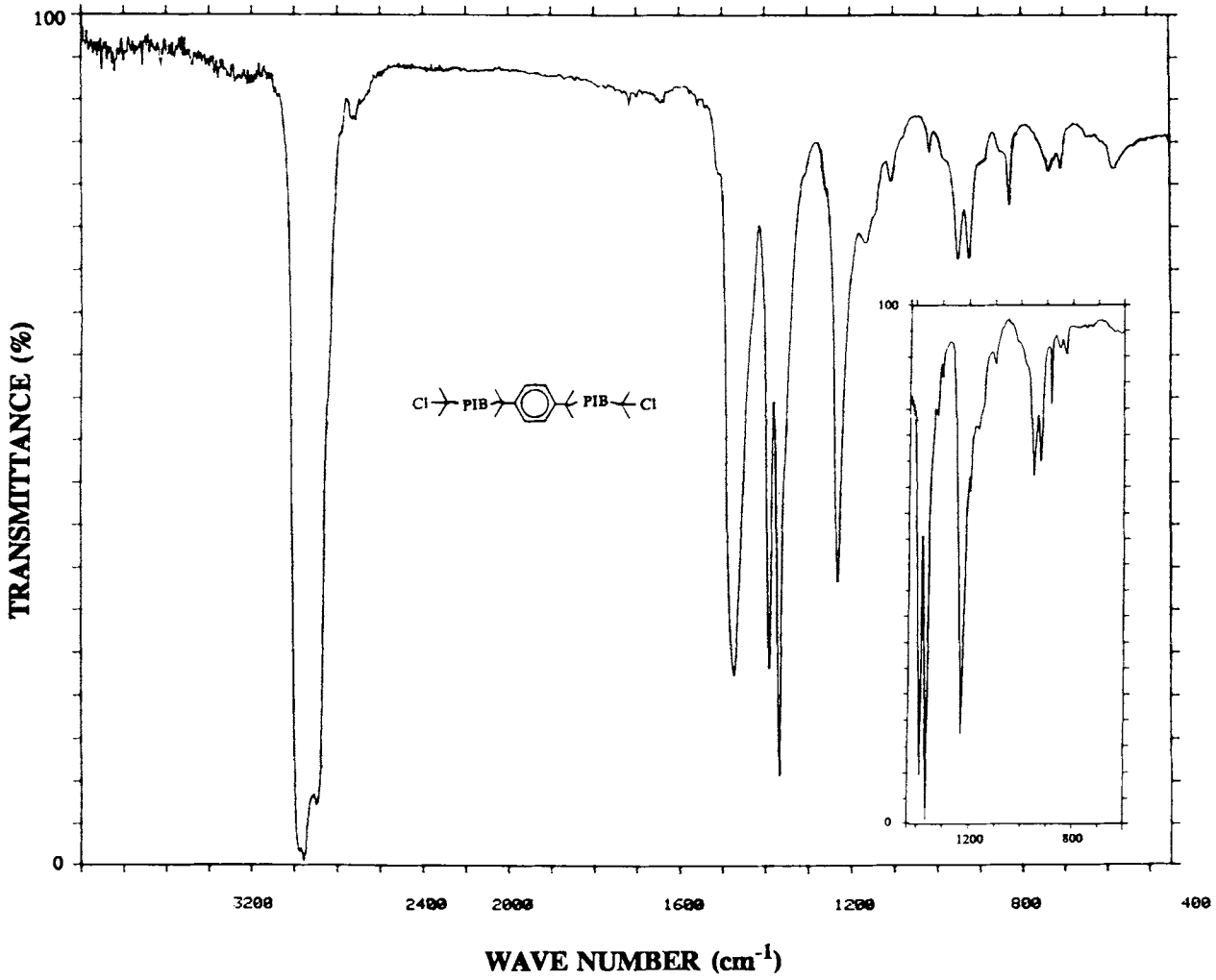

Figure 1 FTIR spectra of α,ω-di(*tert*-chloro)polyisobutylenes, synthesized using: 1,4-Dicumyl alcohol/BCl_3/CH_2Cl_2/−65°C initiating system in the presence of 1-methyl-2-pyrrolidinone and (*inset*) in the absence of 1-methyl-2-pyrrolidinone for isobutylene polymerization.

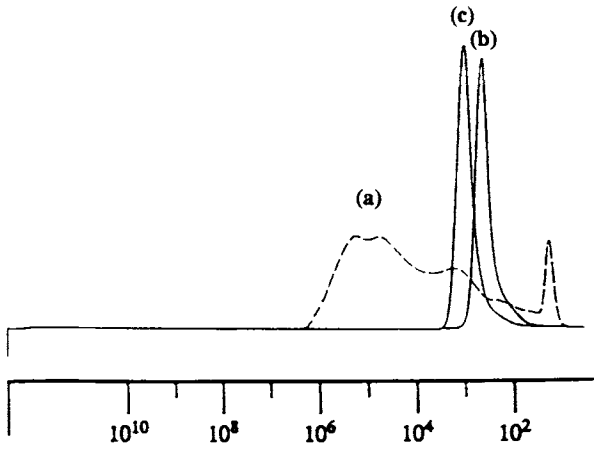

Figure 2 GPC traces of α,ω-di(*tert*-chloro)polyisobutylenes, prepared using the 1,4-dicumyl alcohol/BCl_3/CH_2Cl_2/−65°C initiating system: (a) In the absence of the ED, (b) In the presence of 1-methyl-2-pyrrolidinone (first monomer addition by AMI technique), and (c) In the presence of 1-methyl-2-pyrrolidinone (second monomer addition by IMA technique).

methyl-2-pyrrolidinone, in conjunction with the initiator/BCl_3, has improved the polymer characteristics. The data in Table I demonstrate the beneficial effects of 1-methyl-2-pyrrolidinone on I_{eff} and polydispersity.

The evidence for the elimination of cycloalkylation was provided by the FTIR analyses of the polymers. The strong absorption at 800 cm^{-1},[15] which corresponds to the indanyl ending, appeared in the polymer that was prepared in the absence of the ED as shown in the inset in Figure 1. Interestingly, this absorption totally disappeared (Fig. 1) in the polymer that was prepared in the presence of 1-methyl-2-pyrrolidinone.

As seen in other *living* isobutylene polymerizations,[1-4,14] the data in Table I show the increase in M_n with the weight of the polymer formed. The *living* nature of these polymers (Run Nos. 2 and 3) was further substantiated by their narrow MWD. The absence of any bimodal MWD, when the fresh monomer (Run 3) was added as shown by the GPC traces (b and c) in Figure 2, indicates the absence of *chain transfer* or *termination* during the polymerization. On the other hand, ill-defined MWD was obtained for the polymer, that was synthesized in the absence of the ED, due to protic and uncontrolled initiation, as shown by the GPC trace (a) in Figure 2.

As anticipated, the free ED inhibits the isobutylene polymerization. The species that mediate the living polymerization of isobutylene are ED × BCl_3 complexes that invariably cause the narrowing effect of the MWD, suggesting a trend towards the living polymerization. These observations are in line with the earlier results of Faust et al.[16,17] It has been theorized that the ED × BCl_3 complexes act as proton scavengers and also eliminate the intramolecular alkylation during the IB polymerization.[16,17] However, the exact mechanism as to how the ED prevents cycloalkylation is still obscure.

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