

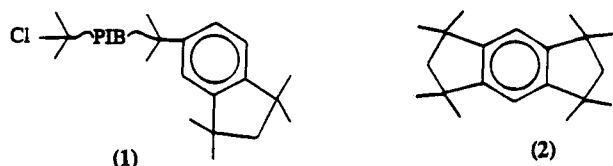
NOTE

Role of Triethylamine in *Living* Carbocationic Polymerization of Isobutylene with 1,4-Dicumyl Alcohol/ BCl_3 Initiating System

INTRODUCTION

The use of deliberately added electron-pair donors (EDs) for the living polymerization of olefins¹ and vinyl ethers² has received a great deal of attention in recent years because of their beneficial effects such as (1) total elimination of protic initiation, (2) prevention of side reactions leading to undesirable cyclic structures, especially with cumyl-based initiators, and (3) controlled initiation resulting in the preparation of narrow molecular weight distribution (MWD) living polymers. A wide variety of EDs such as *N,N*-dimethylacetamide (DMA),^{1,3,4} dimethylsulfoxide (DMSO),^{1,5} ethyl acetate,^{3,4,6} and, more recently, 1-methyl-2-pyrrolidinone^{7,8} have been investigated in conjunction with both aromatic and aliphatic initiators for the living polymerization of isobutylene using the *inifer* concept.⁹

Of the aromatic initiators, 1,4-dicumyl-type initiators (esters, ethers, alcohols, chlorides) have been thoroughly investigated since the initiating work of Kennedy and Smith.⁹ Despite the impressive application for the preparation of α,ω -di(*tert*-chloro)polyisobutylenes, the use of these initiators often suffers cycloalkylation due to the back-biting of the initiator to the active-growing end to form undesirable cyclic structures—the indanyl (**1**) and diindane (**2**) end groups shown below—hampering the clean synthesis of perfect telechelic polymers⁹⁻¹¹:



Herein, we report the use of a tertiary amine, triethylamine, as another potential ED for the living polymerization of isobutylene in conjunction with 1,4-dicumyl alcohol and boron trichloride (BCl_3) in dichloromethane at -65°C , resulting in the synthesis of living α,ω -di(*tert*-chloro)polyisobutylenes of low polydispersities ($M_w/M_n = 1.2$ – 1.3). In these investigations, we chose another efficient ED such as DMA for comparison. Results indicate that triethylamine, like DMA, in conjunction with 1,4-dicumyl alcohol/ BCl_3 is efficient in modulating the con-

trolled initiation, yielding living telechelic polyisobutylenes. To our knowledge, there are no published reports on the use of triethylamine as an ED for the purpose of living polymerization of isobutylene. This paper also demonstrates that the undesirable side reactions such as intramolecular alkylation and protic initiation can be totally eliminated with the proper choice of a select ED such as triethylamine.

EXPERIMENTAL

Materials

1,4-Dicumyl alcohol, obtained through the courtesy of the Goodyear Tire and Rubber Co., was recrystallized from methanol before use and its purity was checked with gas chromatography. Isobutylene (IB), BCl_3 , methanol, potassium *tert*-butoxide, lithium aluminum hydride (LAH), DMA, toluene, and dry dichloromethane (all Aldrich) were used without further purification. Triethylamine (TEA) was refluxed and distilled over anhydrous KOH, and tetrahydrofuran (THF) was distilled over LAH before use.

Methods

Polymer analysis was done using infrared spectroscopy (Perkin-Elmer FTIR spectrometer, Model 1710). Molecular weights of these polymers were determined by a Waters high-pressure GPC (Model 264), equipped with a series of three columns of Lichrogel PS 400, PS 40, and PS 1 (E. Merck) with a particle size of $10\ \mu\text{m}$ and 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.

Synthesis of α,ω -Di(*tert*-chloro)polyisobutylenes

Applying the classical *inifer* method using both *incremental monomer addition* (IMA) and *all-monomer-in* (AMI)

Table I Polymerization of Isobutylene with 1,4-Dicumyl Alcohol/ BCl_3 /ED Initiating Systems Using the *Inifer* Concept

Entry No.	ED	Time (min)	W_p (g)	M_n^a	M_w/M_n	I_{eff}	Remarks
a	None	20	1.10	NA	4.90	NA	Cyclic side products ^b
b	DMA	20	0.80	1770	1.25	102.7	Telechelic ^b
c	TEA	20	0.81	1745	1.29	105.4	Telechelic ^b
d	TEA	40	1.13	2510	1.35	102.3	Telechelic ^b

[IB] = 17.7 mmol; [1,4-Dicumyl alcohol] = 0.44 mmol; [BCl_3] = 7.92 mmol; [ED] = 0.924 mmol; CH_2Cl_2 = 15 mL; temp = -65°C ; addition of IB after 10 min of premixing the initiator/ED with BCl_3 . a and b by AMI method; c and d by IMA method. NA = not available.

^a VPO measurements.

^b FTIR analysis.

techniques,¹² polymerizations were performed in 75 mL culture tubes fitted with mechanical stirrers. Polymerization conditions and the concentration data are listed in Table I. Polymerizations were initiated with the injection of the monomer after 10 min of premixing the initiator with BCl_3 and ED and quenched with the addition of pre-chilled methanol.

RESULTS AND DISCUSSION

Table I lists the conditions and the results of isobutylene polymerizations initiated with 1,4-dicumyl alcohol/ BCl_3 / CH_2Cl_2 in the absence and the presence of the above EDs, TEA, or DMA. Instantaneous polymerization (in a few seconds) of IB in the absence of TEA or DMA with 1,4-dicumyl alcohol and BCl_3 , the formation of an insignificant amount of polymer in the absence of the initiator, and no traces of polymerization in the presence of ED alone are in line with the earlier observations.^{1,7} These results also indicate that the tertiary alcohol is the true initiating species, whereas a free ED inhibits the IB polymerization. Also, slower polymerization (appearance of the polymer was noticed in about 13–15 min) of IB with the initiator/ BCl_3 in conjunction with either TEA or DMA suggests that the presence of ED only modulates the reactivity of active polymerization cations, leading to the controlled initiation by the initiator. The mechanism of initiation is probably similar to that proposed for tertiary ester/ethyl acetate⁴ and aliphatic initiators/DMSO⁵ systems. The "living" nature of this polymerization was demonstrated by the linear increase in M_n with the weight of the polymer formed (entries c and d) and further substantiated by GPC studies. The fact that there are no bimodal distributions of molecular weights when fresh monomer (entry d) was added to the active-polymer recipe, as shown by the GPC traces in Figure 1, indicates the absence of any chain termination or transfer in this polymerization.

Ample evidence for the elimination of cycloalkylation was provided by the FTIR analysis of the polymers. The absence of any noticeable absorption at 800 cm^{-1} in the

polymers, synthesized in the presence of TEA or DMA, explicitly demonstrates the absence of any intramolecular alkylation.⁷ An intense absorption at 800 cm^{-1} corresponding to the indanyl ending appeared in polymer that

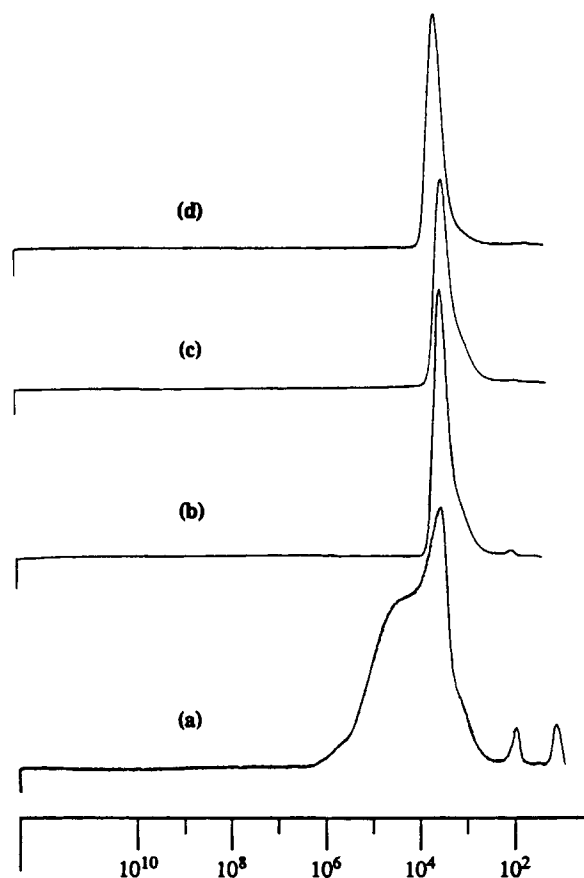


Figure 1 GPC traces of α,ω -di(*tert*-chloro)polyisobutylenes, obtained by the 1,4-dicumyl alcohol/ BCl_3 / CH_2Cl_2 initiating systems at -65°C : (a) in the absence of any ED; (b) in the presence of DMA (by AMI technique) (c) and (d) in the presence of TEA (by IMA technique).

was prepared in the absence of any ED.¹³ Finally, the end-group analysis by FTIR of the dehydrochlorinated polymer (entry **d**) by the well-established method using potassium *tert*-butoxide in dry THF¹⁴ showed the presence of vinylic absorptions. This indirectly proves the end functionality of the prepolymers to be *tert*-chloro groups.

Triethylamine, in conjunction with 1,4-dicumyl alcohol and BCl₃, played a similar role like DMA in IB polymerizations and effectively reduced the MWD (narrowing effect) and molecular weights of the resulting polymers. The use of TEA as an ED also demonstrated the suppression of cycloalkylation and the total elimination of initiation due to protic impurities. All these observations can be rationalized as a result of reduction of cationicity by the stabilization of the polymerization-active species (carbocations) by a suitable ED.

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