A new initiating (minifer) system leading to the synthesis of living telechelic α-cyclohexyl-ω(tert-chloro)polyisobutylenes*

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A new efficient monofunctional initiator transfer (minifer) system, comprising 2-cyclohexyl-2-propanol, BCl_3 and 1-methyl-2-pyrrolidinone, has been investigated for the first time in CH_2Cl_2 diluent at −40°C for the living polymerization of isobutylene. The use of this new minifer system has led to the synthesis of low molecular weight, living (near-monodisperse), new α-cyclohexyl-ω(tert-chloro)polyisobutylenes. The structural analysis of these polymers by ^{13}C n.m.r. spectroscopy confirmed the nature of the head and end groups to be a cyclohexyl and a tert-chloro, respectively. The living nature of these polymers has been demonstrated by kinetic investigations as well as by their low polydispersity ($\bar{M}_w/\bar{M}_n = 1.18–1.43$) values from g.p.c. studies.

(Keywords: living carbocationic polymerization; 2-cyclohexyl-2-propanol; 1-methyl-2-pyrrolidinone; isobutylene; initiator efficiency)

Introduction

Living polymerization proceeds in the absence of termination and chain transfer and is one of the most versatile techniques for synthesizing polymers with well-defined structures, molecular weights and molecular weight distributions (*MWD*s)[1]. Since the discovery of the living anionic polymerization[2,3], living polymerizations have gained both scientific[1,4] and commercial interest[5,6]. Several successful attempts have since been made to find conditions under which a living carbocationic polymerization of olefin monomers could be achieved[7,8]. A conventional non-living carbocationic polymerization can be rendered living by the use of an initiator in conjunction with a selected electron-pair donor (ED). The ED apparently stabilizes and controls the high intrinsic reactivity of otherwise unstable growing polymerization-active carbocations that would, without the ED, lead to undesirable side reactions such as chain transfer, irreversible chain termination, uncontrolled initiation by protic and other impurities[9,10]. Using this concept, Higashimura *et al.* and Kaszas *et al.* have successfully demonstrated the living carbocationic polymerizations of vinyl ethers[9,11] and isobutylene[10], respectively, with proper EDs.

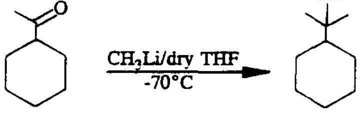
In view of the recent significant developments in living carbocationic polymerizations, especially with the use of EDs[10] such as N,N-dimethylacetamide (DMA) and dimethylsulphoxide (DMSO) and new initiators by Kaszas *et al.* for isobutylene (IB) polymerizations using the classical initiator transfer (inifer) method[12], we have investigated the potential use of another ED, 1-methyl-2-pyrrolidinone, in conjunction with the new initiator, 2-cyclohexyl-2-propanol, for the preparation of well-defined, narrow *MWD*, living polyisobutylenes end-capped with tert-chloro groups. The great advantage of using an alicyclic initiator over an aromatic initiator is that the former initiator does not encounter cycloalkylation, which hampers the synthesis of perfect telechelic polymers as observed with the latter initiators[13]. Additionally, the end group can be modified into unique, new, near-monodisperse network ionomers[14].

In this paper, we report for the first time the use of a 2-cyclohexyl-2-propanol/BCl_3/1-methyl-2-pyrrolidinone/CH_2Cl_2 initiating system for the facile synthesis of living, new α-cyclohexyl-ω(tert-chloro)polyisobutylenes by ED-stabilized living carbocationic polymerization of IB at −40°C. Also presented is the spectroscopic evidence to prove the head and end functionalities by ^{13}C n.m.r. spectroscopy. The living nature of these polymers has been demonstrated by the kinetic investigations as well as by g.p.c. studies.

Experimental

Materials. 2-Cyclohexyl-2-propanol initiator was prepared using acetyl cyclohexane as shown in *Scheme 1*. Isobutylene (Aldrich) was used by condensing it under a dry nitrogen atmosphere. Methylene chloride was distilled over CaH_2 before use. Boron trichloride, acetyl cyclohexane, methyl lithium, anhydrous 1-methyl-2-pyrrolidinone (M-pyrol), lithium aluminum hydride (LAH), potassium tert-butoxide (t-BuOK), methanol and hexane (all Aldrich) were used as received. Tetrahydrofuran (THF) was distilled over LAH and toluene was distilled before use.

Synthesis of 2-cyclohexyl-2-propanol. In the process described here, acetyl cyclohexane (2.0 g, 0.0158 mol)



Scheme 1

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and dry THF were placed in a 100 ml two-necked flask fitted with a septum, a magnetic stir bar and an inlet for nitrogen. Methyl lithium (0.52 g, 0.0238 mol) was slowly added dropwise to acetyl cyclohexane at $-70°C$ and the reaction was continued for 2 h[15]. The course of the reaction was followed with a gas chromatograph. The reaction was stopped by the slow addition of aqueous saturated ammonium chloride solution. The product was extracted with ether and washed with water until neutral. The ether extract was dried over anhydrous Na_2SO_4 and evaporated *in vacuo* (yield 72%). The product was chromatographed through neutral alumina to afford pure 2-cyclohexyl-2-propanol (yield 64%).

Figure 1 shows the ^{13}C n.m.r. spectrum of 2-cyclohexyl-2-propanol. ^{13}C n.m.r. data (δ): (a) 26.21, (b) 26.45, (c) 26.64, (d) 27.31, (e) 49.09 and (f) 72.89.

Polymer syntheses were carried out as shown in *Scheme 2* using the inifer method.

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[8]. Polymerization conditions are listed in *Table 1*. 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 anhydrous Na_2SO_4 and filtered. The polymer was recovered by evaporating the solvent by rotavap and dried *in vacuo*.

Polymer analyses. The i.r. spectrum was recorded on a Perkin Elmer Fourier transform i.r. spectrometer (Model 1710). ^{13}C n.m.r. spectra were taken by a Jeol 400 MHz spectrometer using $CDCl_3$ solutions.

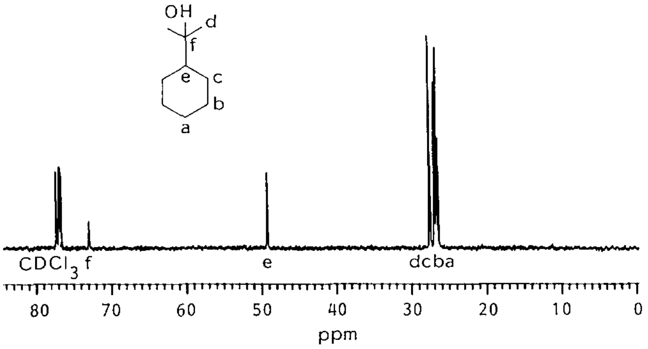


Figure 1 ^{13}C n.m.r. spectrum of 2-cyclohexyl-2-propanol

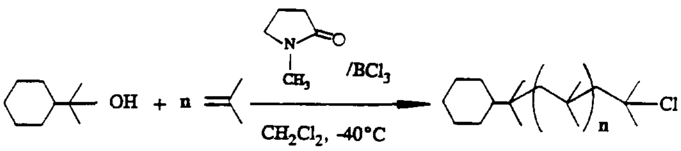
Molecular weights ($\bar{M}_w$) and *MWD*s of these polymers were determined using a Waters (model 264) gel permeation chromatograph provided with a differential refractometer (Waters, model 401) for detection and interfaced with a gas chromatograph integrator (HP 3396A) for recording. The calibration curve was made with polystyrene standards in degassed THF, using a series of Lichrogel columns of PS400, PS40 and PS1 (E. Merck) having a particle size of 10 μm.

The number average molecular weights ($\bar{M}_n$) of the polymers were determined in toluene using a Wescan Instruments (Model 232A) vapour pressure osmometer calibrated with sucrose octaacetate.

Results and discussion

Chen *et al.*[16] have recently demonstrated that both DMA and DMSO are efficient EDs in conjunction with both aliphatic and aromatic tert-alcohols and with either BCl_3 or $TiCl_4$ for the living polymerization of IB. We selected 2-cyclohexyl-2-propanol as the initiator for the preparation of terminally functionalized (telechelic) polyisobutylenes, as there has been no report in the literature concerning its application as an initiator for IB polymerization. The choice of M-pyrol as an ED, on the other hand, is based on its dielectric constant (32), which lies close to the dielectric constants of the other efficient EDs such as DMA (37.78) and DMSO (46.68)[17].

When the monomer was mixed with BCl_3 in CH_2Cl_2, only an insignificant amount of the polymer was formed, most likely because of the protic impurities. On the other hand, instantaneous polymerization was observed (< 1 min) when 2-cyclohexyl-2-propanol was used in conjunction with BCl_3. In the absence of BCl_3 coinitiator, control experiments indicated no sign of IB polymerization in the presence of either M-pyrol or DMA or 2-cyclohexyl-2-propanol alone. After 10 min of premixing



Scheme 2

Table 1 Isobutylene polymerization using 2-cyclohexyl-2-propanol/BCl_3/ED systems[a]

Sample no.[b]	ED	Time (min)	W_p (g)	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[d]	I_{eff} (%)
1	M-Pyrol	30	0.47	1350	1.18	82.5
2	M-Pyrol	60	0.91	2460	1.29	87.7
3	M-Pyrol	90	1.71	4410	1.37	91.9
4	M-Pyrol	120	2.34	6030	1.43	92.0
5	DMA	30	0.50	1476	1.19	80.6
6	–	30	0.69	–[e]	6.52	–[e]

[a] [2-Cyclohexyl-2-propanol] = 0.4218 mmol; [IB] = 16.87 mmol; [BCl_3] = 5.22 mmol; [1-methyl-2-pyrrolidinone] = 0.4218 mmol; CH_2Cl_2 = 20 ml; $-40°C$

[b] Samples 1–4 by IMA method, 5 and 6 by AMI method

[c] Obtained by vapour pressure osmometry measurements

[d] Obtained by g.p.c. measurements

[e] Not available

Scheme 3

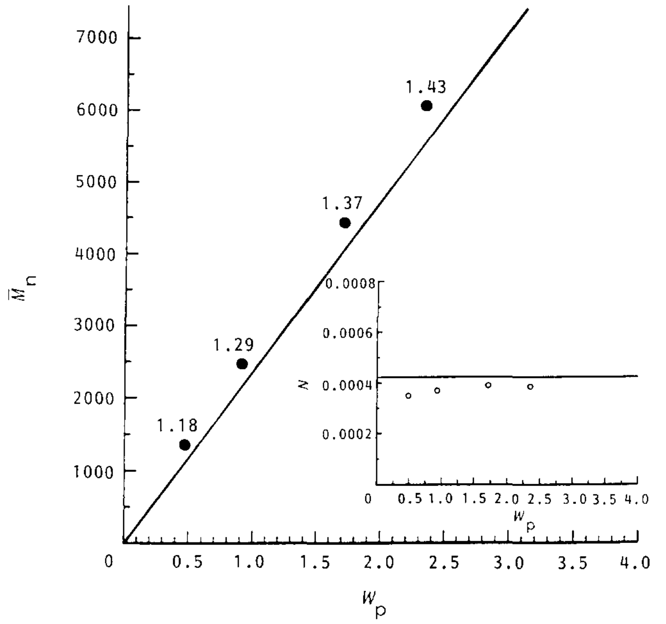


Figure 2 $\bar{M}_n$ and N, the number of polyisobutylene chains (inset), *versus* the weight of the polymer (W_p) formed by 2-cyclohexyl-2-propanol/IB/BCl_3/1-methyl-2-pyrrolidinone system at −40°C by the incremental monomer addition technique (IMA); [2-cyclohexyl-2-propanol] = 0.4218 mmol; [IB] = 16.87 mmol; [BCl_3] = 5.22 mmol; [1-methyl-2-pyrrolidinone] or [DMA] = 0.4218 mmol; CH_2Cl_2 = 20 ml; 30 min. Solid lines represent theoretical values. Numbers indicate $\bar{M}_w/\bar{M}_n$ values

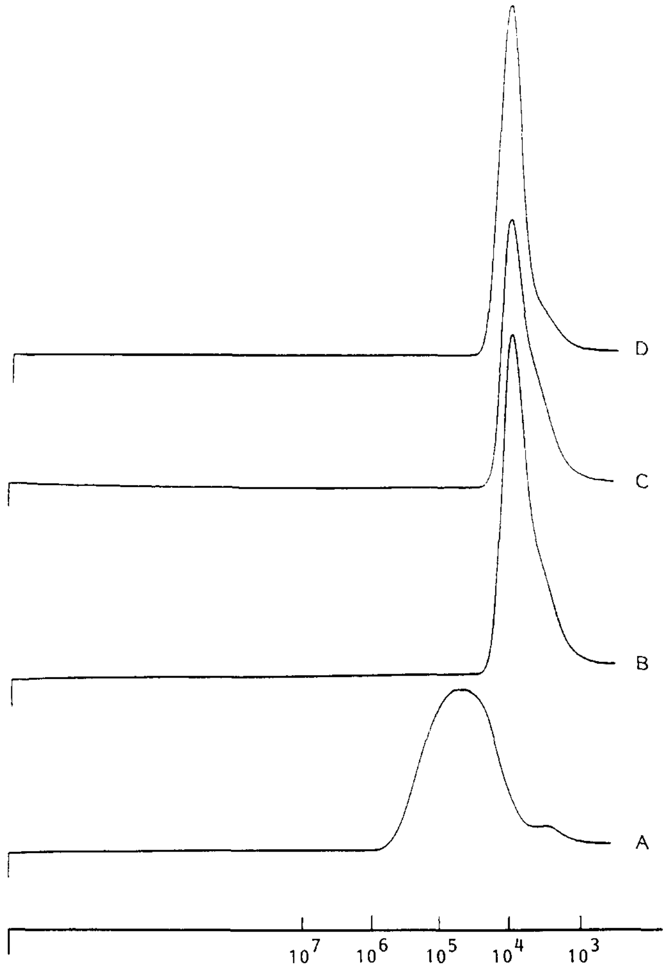


Figure 3 G.p.c. (RI) traces of polyisobutylenes prepared by the 2-cyclohexyl-2-propanol/IB/BCl_3/CH_2Cl_2 system: (A) in the absence of any ED and (B) in the presence of DMA by all monomer in (AMI) technique, and (C and D) in the presence of 1-methyl-2-pyrrolidinone using incremental monomer addition (IMA) technique. Reaction conditions as in *Figure 2*

the initiator with BCl_3 in CH_2Cl_2, polymerization was commenced by the addition of the monomer. However, polymerization in the presence of M-pyrol or DMA was very slow by cationic polymerization standards, indicating that both EDs effectively modulated the reactivity of polymerization-active carbocations. The conditions and results of IB polymerization initiated with 2-cyclohexyl-2-propanol/BCl_3 in the absence of any ED and in the presence of M-pyrol or DMA in CH_2Cl_2 at −40°C are listed in *Table 1*.

The mechanism of initiation of these polymerizations is analogous to that proposed for any tert-alcohol/BCl_3/DMA or DMSO initiated IB polymerizations[16]. Initiation occurs in a three-component system, organic tertiary alcohol/BCl_3/IB, regardless of the introduction sequence of reagents[8]. The addition of BCl_3 to 2-cyclohexyl-2-propanol initially transforms it into the corresponding chloride. The excess BCl_3, used in these polymerizations, apparently ionizes 2-cyclohexyl-2-propyl chloride. In line with the earlier conclusions of Chen *et al.*[16], the end-capping of these polymers by tert-chloro groups is visualized to involve reversible termination as shown in *Scheme 3*.

The diagnostic proof for the living nature of these polymers has been provided by kinetic experiments and the results are shown in *Figure 2*. The values of $\bar{M}_n$ increase linearly with W_p (weight of the polymer formed) with the increasing addition of monomer, while the plot (inset) of N (number of PIB molecules formed, obtained from $g/\bar{M}_n$ *versus* W_p is horizontal. Further evidence for the living nature of this polymerization has been provided by g.p.c. studies. The g.p.c. traces of the samples prepared by the IMA technique are shown in *Figure 3*. The increase in molecular weights and narrow *MWD*s of the resulting polymers with increasing monomer addition in the presence of M-pyrol by the diagnostic IMA technique explicitly suggest the living nature of these polymers. On the other hand, the *MWD* of the polymer that was prepared in the absence of either M-pyrol or DMA is wider as a result of the protic initiation. Thus, the addition of M-pyrol or DMA not only eliminated the side reactions triggered by the presence of protic impurities, but also showed a very significant narrowing effect on the *MWD* of the resulting polymers.

The nature of head and end groups and the strong evidence for the absence of chain transfer in this type of polymerization have been furnished by the ^{13}C n.m.r. spectroscopic study, as shown in *Figure 4*, of a

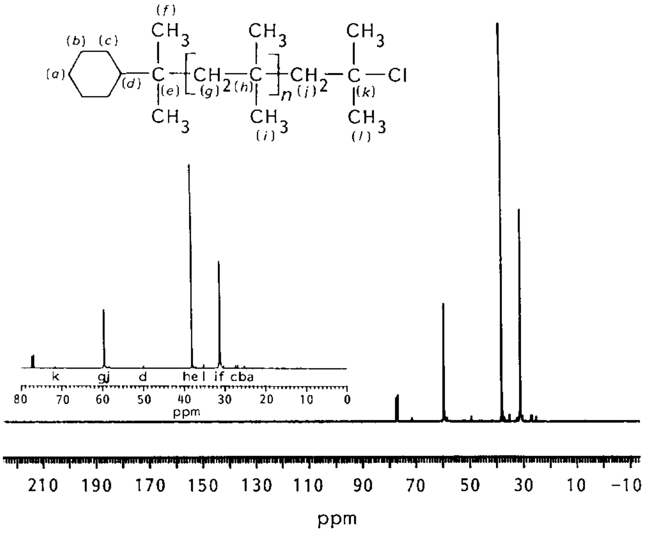


Figure 4 ^{13}C n.m.r. spectrum of α-cyclohexyl-ω(tert-chloro)polyisobutylene, (sample 2, see *Table 1* for experimental conditions) prepared by the 2-cyclohexyl-2-propanol/IB/BCl_3/1-methyl-2-pyrrolidinone system in CH_2Cl_2

representative polymer (second sample of IMA method) prepared using this monofunctional initiator transfer (minifer) system. The appearance of the signal at 71.5 ppm corresponds to the tertiary carbon bonded to the terminal chloro group ($-C(CH_3)_2Cl$) while the signals between 25.0 ppm and 27.5 ppm correspond to the cyclohexyl group. Thus, the nature of the head and the end groups are a cyclohexyl and a tert-chloro, respectively. Absence of any signals in the 110–150 ppm region corresponding to the olefinic carbons, which could have appeared if there had been any chain transfer during the polymerization, confirms the absence of chain transfer in these polymerizations.

The end group functionality was also indirectly determined by the dehydrochlorination of the prepolymer (second sample in *Table 1* by the IMA method) with t-BuOK[18] and the resulting polymer was characterized by Fourier transform i.r. spectroscopy. The appearance of weak asymmetric stretching at 3070 cm^{-1}, symmetric stretching vibrations at 1641 cm^{-1} together with a strong doublet at 1049, 1011 and 851 cm^{-1} as a result of the out-of-plane bending vibrations corresponding to the characteristic olefinic absorptions of the resulting dehydrochlorinated polymer, α-cyclohexyl-ω(isopropenyl)polyisobutylene, confirms the nature of the end group to be a tert-chloro in the corresponding prepolymer. Additionally, it shows the characteristic absorptions of νC–H (aliphatic asymmetric and symmetric stretching vibrations) in the range of 2850–2985 cm^{-1}, δC–H (scissoring of $-CH_2-$ and asymmetric swinging of $-CH_3$) at 1465 cm^{-1}, 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 $-CH_2-$), which confirm the repeating units ($-CH_2-C(CH_3)_2-$) in polyisobutylenes.

According to these data, 2-cyclohexyl-2-propanol/BCl_3/1-methyl-2-pyrrolidinone is an efficient minifer system for the living polymerization of IB at −40°C yielding narrow *MWD* α-cyclohexyl-ω(tert-chloro)polyisobutylenes.

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