A Novel Functional Initiator for the Synthesis of a Living, New Asymmetric Telechelic Poly(isobutylene)

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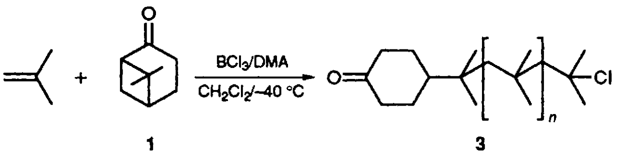
(+)-(1*R*)-Nopinone **1**, in conjunction with a Lewis acid and an electron donor (*N,N*-dimethylacetamide or triethylamine) in CH_2Cl_2, initiates the polymerisation of isobutylene at −40 °C resulting in the formation of a new α,ω-asymmetric telechelic poly(isobutylene) of low polydispersity.

α,ω-Asymmetric telechelic poly(isobutylenes), X-PIB-Y, **2**, which bear dissimilar functional groups at both chain ends, represent a very interesting class of materials as they allow selective end-group functionalisation into unique, new materials for a number of applications such as macromonomers, block polymers, ionomers and biomedical materials.[1] Although the preparation of **2** is strenuous, such well-defined asymmetric telechelic PIB prepolymers, capped with various functional groups, have recently been the subject of much interest since the introduction of the 'inifer' concept by Kennedy *et al.*[2] for living carbocationic polymerisation of isobutylene (IB) using polyfunctional *tert*-ester, ether, halide, alcohol and lactone.[3] Here, we describe the application of **1** as an efficient novel functional initiator for the polymerisation of IB with BCl_3 in conjunction with either *N,N*-dimethylacetamide (DMA) or triethylamine (TEA) in dichloromethane at −40 °C for the synthesis of a new α-(4-cyclohexanone)-ω-(chlorodimethyl)poly(isobutylene) **3** of low polydispersity as shown in Scheme 1.

In the present study, use has been made of a bicyclic ketone, **1**, which undergoes acid catalysed ring-opening to form the corresponding 4-(1′-chloro-1′,1′-dimethyl)cyclohexanone, **4**.[4] If this reaction proceeds in conjunction with BCl_3, it should be possible to carry out the carbocationic polymerisation of the added IB monomer. To our knowledge, this is the first report on the application of **1** as an efficient *mono*functional *ini*tiator trans*fer* ('minifer') agent for the synthesis of a new polymer, **3**. For comparison purposes, we polymerised IB by the 4-(1′-hydroxy-1′,1′-dimethyl)cyclohexanone **5**/BCl_3 initiating system, which also resulted in **3**.[5]

The polymerisation of IB was carried out as follows: (*a*) To a magnetically stirred solution of the initiator **1** or **5** (0.393 mmol) in dry dichloromethane (20 ml), prechilled IB



Scheme 1

Table 1 Polymerisation of isobutylene (IB) by (i) **1**/BCl_3, (ii) **1**/BC_3/DMA or TEA and (iii) **5**/BCl_3 initiating systems in CH_2Cl_2 at −40 °C

Sample no.	Initiating system	t/min	M_p/g	M_n[a] (Found)	Polydispersity (M_w/M_n)[b]	I_{eff}[b]
1	**1**/BCl_3	30	0.61	2601	4.95	59.60
2	**1**/BCl_3/DMA	30	0.45	1145	1.31	99.87
3	**1**/BCl_3/DMA	60	1.10	2784	1.42	100.40
4	**1**/BCl_3/TEA	30	0.43	1120	1.29	98.82
5	**1**/BCl_3/TEA	60	1.09	2830	1.46	98.53
6	**5**/BCl_3	30	0.54	3257	11.24	42.13

[a] By GPC measurements. [b] (M_p × 100/M_n × [initiator]), samples 1, 2, 4 and 6 by the all monomer in (AMI) technique, and samples 3 and 5 by the incremental monomer addition (IMA) technique.

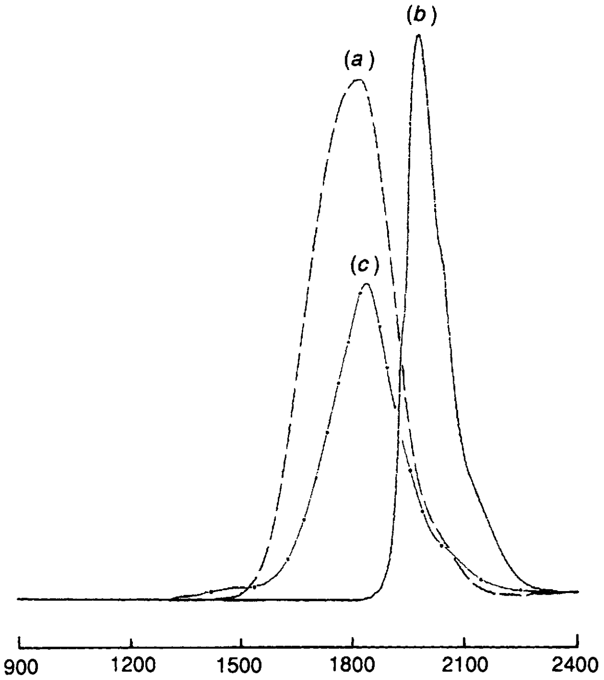


Fig. 1 Representative GPC elution (RI) traces of α-(4-cyclohexanone)-ω-(chlorodimethyl)poly(isobutylene) **3**, synthesised by the initiating systems in CH_2Cl_2 at −40 °C: (*a*) **1**/BCl_3 (sample 1); (*b*) **1**/BCl_3/DMA (sample 2); and (*c*) **5**/BCl_3 (sample 6)

(11.8 mmol) was added under a dry nitrogen atmosphere. After allowing the contents to stir for 15 min, polymerisation was started by the addition of BCl_3 (7.9 mmol) at −40 °C and continued for the desired time, Table 1. Polymerisation was then terminated by the addition of prechilled methanol (3 ml). The solvents were evaporated and the resulting polymer was dissolved in (olefin-free) hexanes. After washing the polymer with water until neutral, it was dried over anhydrous Na_2SO_4. Evaporation of the solvent furnished the polymer, which was dried *in vacuo* to a constant mass. (*b*) While maintaining the same molar ratio of the reactants under identical polymerisation conditions, living polymerisation of IB was effected by the addition of BCl_3 to the premixed solution of initiator, monomer, and DMA or TEA (0.393 mmol) in CH_2Cl_2.

The dry and liquid polymers were characterised by the FTIR and ^{13}C NMR spectroscopic methods.† The functionalities, 'α-(4-cyclohexanone)' head-group (δ 212.1) and the 'ω-(chlorodimethyl)' end-group (δ 71.6), were identified in polymers **3** by ^{13}C NMR spectroscopy. As shown by the gel permeation chromatography (GPC) traces of the polymers in Fig. 1, the polymer (sample 2), prepared by the novel **1**/BCl_3/DMA initiating system, shows all the characteristics of a well-defined living polymer with a low polydispersity or narrow molecular mass distribution (MMD) and the polymer (sample 3) shows the progressive increase in molecular mass with increasing monomer to initiator ratio, Table 1. These results were further corroborated with the **1**/BCl_3/TEA initating system as given in Table 1.

As is evident from the results of the present study, our proposition has proved to be correct. The true initiating species in this polymerisation is the *in situ* formed **4**, effecting the carbocationic polymerisation of added IB monomer in conjunction with BCl_3.[5] The following observations prove the advantages of the novel functional initiator, **1**: (*i*) application of **1** as an initiator for the polymerisation of IB in conjunction with both BCl_3 and either electron donor resulted in the preparation of a living, new, functional polymer, **3**; (*ii*) the use of our novel **1**/BCl_3 initiating system (sample 1) was found to reduce the protic initiation of the monomer as compared with the polymer resulting from the **5**/BCl_3 initiating system (sample 6) in the absence of any electron donor such as DMA for the preparation of **3** at the identical polymerisation conditions[5] as shown by the GPC results in Fig. 1; and (*iii*) the initiator efficiency and yield of **3** were found to be higher for the **1**/BCl_3 initiating system (sample 1) than for the **5**/BCl_3 initiating system (sample 6), Table 1.

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† All new polymers were characterised on the basis of the spectroscopic data: Selected spectroscopic values for polymer **3** are as follows: (**3**, samples 2–5): IR (neat) ν/cm^{-1} 1726, 1390, 1365, 1232, 955, 925; ^{13}C NMR ($CDCl_3$, 400 MHz) δ 31.5, 35.5, 38.4, 59.8, 71.5, 211.9.

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