

Synthesis of isobutenyl-telechelic polyisobutylene by functionalization with isobutenyltrimethylsilane

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(Received 15 December 1995; revised 9 August 1996)

Isobutenyl-telechelic polyisobutylenes (PIBs) were synthesized by reacting *tert*-chlorine-telechelic and living PIBs with isobutenyltrimethylsilane (IBTMS) in the presence of TiCl_4 in CH_2Cl_2 /hexane (40/60 v/v) solvent mixtures at -78°C . In order to obtain PIB oligomers, living polymerization of isobutylene was induced by the di-(2-hydroxy-2-propyl)-5-*tert*-butylbenzene (*t*BuDiCumOH)/ BCl_3 combination in CH_2Cl_2 followed by addition of required amounts of hexane and TiCl_4 to avoid polymer precipitation and permanent termination. Although quantitative end-quenching of living PIB was achieved with IBTMS, chain coupling between the living PIB chains and isobutenyl-ended polymers also occurred. This side reaction was avoided by isobutenylation of *tert*-chlorine-telechelic PIB with IBTMS in the presence of TiCl_4 . The resulting isobutenyl-telechelic PIB contains exclusively *exo*- $\text{CH}_2\text{-C}(\text{CH}_3)=\text{CH}_2$ endgroups, and is free from $\text{-CH}=\text{C}(\text{CH}_3)_2$ *endo* olefins usually obtained in small quantities ($\sim 3\text{--}8\%$ of total double bonds) as a side product of other methods used in the past. © 1997 Elsevier Science Ltd.

(Keywords: telechelic; polyisobutylene; functionalization)

INTRODUCTION

Syntheses of a variety of useful telechelic polyisobutylenes (PIBs) carrying reactive termini have been reported during the past 15 years (for recent reviews see refs 1–5). The so-called inifer method⁶ led to the preparation of telechelic PIBs with *tert*-chlorine endgroups upon quenching the polymerization with methanol. Quenching living polymerizations of isobutylene with excess nucleophiles also yielded *tert*-chlorine endgroups^{7–10}. Quantitative dehydrochlorination of the *tert*-chlorine chain end by a strong base, such as *t*BuOK¹¹ or CH_3ONa ¹², was claimed to yield 2-methyl-2-propenyl (isobutenyl)-telechelic PIBs. Another type of olefin terminated polymers, allyl-telechelic PIBs, was obtained by allylation of *tert*-chlorine-terminated PIBs¹³, and later by one-pot end-quenching of living PIB chains by allyltrimethylsilane (ATMS)^{9,10}. Due to the necessity of polymer purification followed by dehydrochlorination of *tert*-chlorine-telechelic PIBs in refluxing dry tetrahydrofuran (THF) for a relatively long time (16–20 h) in order to obtain isobutenyl termini, allyl end-quenching is a simpler, faster and more economic process to prepare olefin-ended PIB¹⁴. Both the isobutenyl and allyl endgroups can be quantitatively converted into hydroxyl-telechelic PIBs by regioselective hydroboration followed by oxidation^{9,10,15}. Telechelic PIBs with unsaturated or hydroxyl endgroups are versatile

starting materials for the preparation of various telechelics¹ and other polymeric products, such as polyurethanes^{10,16,17} polyepoxies^{10,18}, endless ionomers¹⁹, amphiphilic networks^{20–24}, and thermally reversible supramolecularly ordered assemblies²⁵.

However, as recent investigations^{26–28} have indicated, dehydrochlorination of *tert*-chlorine terminated PIBs with *t*BuOK leads not only to $\text{-CH}_2\text{-C}(\text{CH}_3)=\text{CH}_2$ *exo*, but $\sim 3\text{--}8\%$ $\text{-CH}=\text{C}(\text{CH}_3)_2$ *endo* olefinic endgroups as well. The reactivity of these terminal groups are significantly different in certain subsequent chain end derivatization reactions, such as hydroboration^{1,9,10,15} for obtaining terminal hydroxyl group or hydroformylation²⁷ for the preparation of aldehyde endgroup. Therefore, these reactions with PIBs containing less than 100% isobutenyl termini cannot yield exact hydroxyl- or aldehyde-telechelic PIBs. Because of the importance of exact isobutenyl-telechelic PIBs, attempts have been made by us to investigate simpler, less laborious and better synthetic methods for the preparation of this polymer with more precise *exo* olefinic endfunctionality than dehydrochlorination^{11,12} of *tert*-chlorine chain ends. This study concerns direct functionalization efforts to obtain isobutenyl-terminated PIB by using isobutenyltrimethylsilane (IBTMS) as functionalizing agent.

EXPERIMENTAL

Materials

The preparation of IBTMS was carried out by a modified procedure based on two previously published methods^{29,30} for the synthesis of the corresponding allyl

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derivative. First, isobutenyltrichlorosilane was prepared in a stirred 1000 ml three-necked round-bottom flask equipped with a reflux condenser, dropping funnel and gas inlet–outlet. Triethylamine (37.04 g, Aldrich, 99%, purified by refluxing with *p*-toluenesulfonylchloride for 3 h, distilled, dried over calcium hydride and distilled again before use), 4,4-dimethylaminopyridine (4.29 g, Aldrich, used as received), cuprous chloride (2.02 g, Merck, 98% purified by dissolving in 37% hydrochloric acid and precipitated by dilution with water, filtered, washed with ethanol and ether and dried *in vacuo* at room temperature), and diethyl ether (200 ml, freed from peroxides by washing with ferrous sulfate, dried over magnesium sulfate and calcium hydride, and distilled) were added to the three-necked flask, and cooled to 0°C by an ice bath. A mixture of 40 ml (0.4 mol) trichlorosilane (Aldrich, used as received), and 44.4 ml (0.44 mol) 3-chloro-2-methylpropene (isobutenyl chloride) (Aldrich, used as received) was added from the dropping funnel during 1 h under a dry nitrogen atmosphere. A large amount of white precipitate was formed. The mixture was allowed to warm-up to room temperature and was then stirred for 20 h. The total liquid phase was transferred through a transfer tube to a 500 ml flask under exclusion of moisture. The diethyl ether was distilled off, and 40 ml isobutenyltrichlorosilane was then collected at 141°C by further distillation.

Isobutenyltrimethylsilane was prepared by adding 40 ml isobutenyltrichlorosilane dropwise to a 500 ml flask containing 300 ml methylmagnesium bromide solution (3.0 M in diethylether, Aldrich) at 0°C during 1 h under stirring. A white precipitate was formed gradually. After stirring for 24 h at room temperature, the reaction mixture was poured carefully into a solution of 1000 ml ice–water mixture containing 40 g ammonium chloride. The organic layer was separated and the remaining aqueous phase was extracted twice with diethyl ether. After washing the organic phase with water until neutral, it was dried with anhydrous magnesium sulfate overnight. After filtering the diethyl ether was distilled off, and the product was collected at 110–111°C. Final distillation on a packed column yielded 12 ml of pure IBTMS (b.p. 110.5°C, 98.5% pure by gas chromatography (g.c.)). ¹H nuclear magnetic resonance (n.m.r.): Si(CH₃)₃ singlet at δ = 0 ppm (9H), –CH₂–Si singlet at δ = 1.5 ppm (2H), CH₃ singlet at δ = 1.7 ppm (3H), H₂C = C doublet at δ = 4.4 ppm (1H) and δ = 4.6 ppm (1H).

2-Chloro-2,4,4-trimethylpentane (TMP-Cl) was obtained by hydrochlorination of 2,4,4-trimethyl-1-pentene (Fluka, >98% used as received) with hydrogen chloride gas in dry dichloromethane at 0°C. After washing, neutralization, drying and evaporation of the solvent, TMP-Cl was isolated by distillation under reduced pressure. ¹H n.m.r.: (CH₃)₃–C: δ = 1.04 ppm (9H), –CH₂–: δ = 1.87 ppm (2H), –(CH₃)₂C–Cl: δ = 1.65 ppm (6H).

Di-(2-hydroxy-2-propyl)-5-*tert*-butylbenzene (*t*BuDi-CumOH) was prepared as described³¹.

Model experiments with TMP-Cl

Model reactions with TMP-Cl were carried out under identical conditions to living cationic polymerizations of isobutylene at –78°C in 25 ml round bottom flasks equipped with magnetic stirrer. In experiment 1 (Exp. 1), 2.5 × 10^{–3} mol TMP-Cl were dissolved in 10 ml dichloromethane, and 5 × 10^{–3} mol IBTMS and 5.5 × 10^{–3} mol BCl₃ (Aldrich, 1 M in dichloromethane) were added. In

another experiment (Exp. 2), 5.0 × 10^{–3} mol TMP-Cl were dissolved in 10 ml dichloromethane and 5 × 10^{–3} mol IBTMS and 10^{–2} mol TiCl₄ were added. The reactions proceeded for 3 h at –78°C, after which the reaction mixtures were allowed to warm up to room temperature and stirred for an additional 20 h, and then the reactions were quenched with 100 ml saturated aqueous NaHCO₃ solution. After extraction with diethyl ether and drying with magnesium sulfate, the diethyl ether was stripped off and the remaining liquids were analysed by ¹H n.m.r.

Polymerization, end-quenching and end-functionalization

Polymerizations and experiments for end-quenching of the living polymer were carried out using conventional laboratory techniques with rubber capped glassware and performing all transfers through transfer needles as previously described³². The living polymerization of isobutylene (IB) was carried out in a round bottom flask equipped with a magnetic stirrer and closed with either a rubber septum or a three-way stopcock, one outlet of which was connected to an inert gas manifold, the other outlet being closed with a septum. First, initiator (*t*BuDiCumOH), solvent (dichloromethane), *N,N*-dimethylacetamide (DMA) and 2,6-di-*tert*-butylpyridine (DtBP) proton trap were transferred to the reactor. After cooling the reaction mixture with an isopropanol–dry ice bath for 1 h at –78°C, pre-chilled (–78°C) isobutylene was added with a syringe, and cooling and mixing was continued for another 10 min. Pre-chilled BCl₃ (Aldrich, 1 M in dichloromethane) was added to initiate the polymerization, which was allowed to progress for 1 h. Then pre-chilled hexanes and TiCl₄ solution were added, followed by charging the pre-chilled end-quenching agent, IBTMS or allyltrimethylsilane (ATMS; Aldrich, used as received). Samples from the reaction mixture were withdrawn at different times through a double tipped needle and poured into a saturated sodium bicarbonate solution. After separation, the organic phase was washed with water until neutral, dried with anhydrous magnesium sulfate, filtered and the solvents were evaporated. The polymer was redissolved in a small amount of hexanes, precipitated into methanol, and dried *in vacuo* at room temperature.

In case of the end-functionalization of *tert*-chlorine-ended PIB, 0.15% polymer ($M_n = 2100$) was dissolved in 25 ml dichloromethane/hexanes solvent mixtures (40/60 v/v). After cooling this solution to –78°C, 1.54 × 10^{–3} mol TiCl₄ solution and 1.38 × 10^{–3} mol IBTMS were added and the reaction was allowed to occur for 83 min. The work-up of the resulting polymer was carried out as described above for polymers obtained by end-quenching of living PIB chains.

Characterizations

¹H n.m.r. analyses were made by a Bruker AC 250 MHz instrument. Molecular weight distribution and average molecular weights were determined by gel permeation chromatography (g.p.c., Waters pump Model 510, Waters R403 differential refractometer, Nucleosil columns 100 Å–3 μ, 200 Å–5 μ, 500 Å–5 μ, THF eluent) calibrated with polyisobutylene standards.

RESULTS

Model experiments with TMP-Cl

Orienting model experiments were carried out with

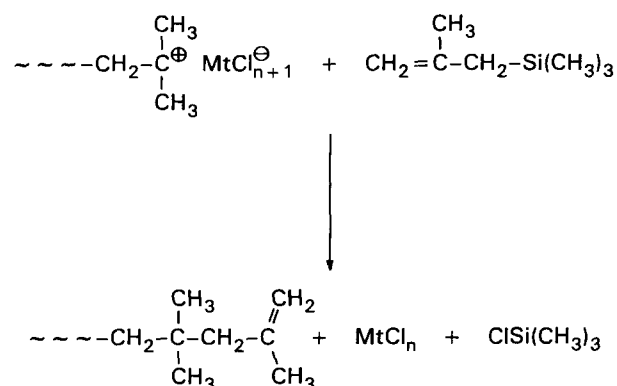
TMP-Cl which mimics the endgroup structure of *tert*-chlorine terminated PIB and the living chain ends upon addition of BCl_3 or TiCl_4 Lewis acids. These reactions were carried out in order to investigate which Lewis acid (BCl_3 or TiCl_4) would be more beneficial for the functionalization reaction with IBTMS. Allylation studies with ATMS indicated that BCl_3 is not a suitable coinitiator to obtain allyl-telechelic PIBs, whereas using TiCl_4 yielded quantitative allylation of either TMP-Cl³³ or *tert*-chlorine-ended PIB¹³ and living PIB chains^{9,10}.

The desired reaction product between TMP-Cl and IBTMS, 2,4,4,6,6-pentamethyl-1-heptene (PMH) is expected to provide ^1H n.m.r. signals similar to that characteristic of the isobutenyl-ended PIB obtained by dehydrochlorination of *tert*-chlorine-terminated chains^{11,12,34}. It was found that olefin signals at 4.52 and 4.78 ppm corresponding to the isobutenyl groups ($-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}_2$) appear in the presence of both BCl_3 and TiCl_4 . However, only a negligible signal was observed at 1.38 ppm characteristic of the methylene protons next to the isobutenyl group ($-\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{C}(\text{CH}_3)=\text{CH}_2$), when the reaction was carried out in the presence of BCl_3 . In contrast, good correlation was obtained between the ^1H n.m.r. signals of these methylene protons and the olefinic protons in the isobutenyl group in experiment 2, i.e. in the presence of TiCl_4 . Thus the results of model experiments indicated that the functionalization reaction with IBTMS for PIB should be carried out in the presence of TiCl_4 .

End-quenching of living PIB chains with IBTMS

In line with the results of model experiments, attempts to functionalize by end-quenching with IBTMS living PIB chain ends obtained by using *t*BuDiCumOH/ BCl_3 initiating system failed. After 2 h reaction time only 8% of the chains were converted into isobutenyl endgroups. This finding, and unsuccessful allylation^{13,33} of *tert*-chlorine-ended PIB by ATMS in the presence of BCl_3 , are most likely due to the relatively high nucleophilicity of the BCl_4^- gegenion leading to faster ion collapse than to isobutenylation (or allylation) and to side reactions of the excess BCl_3 with the silicon compounds. Since living carbocationic polymerization of vinyl monomers is a quasiling process^{1,35,36} with equilibrium between active (propagating) and dormant (terminated) chains, the first process yields relatively low concentrations of the active chains. On the other hand, side reactions, such as addition of BCl_3 to the olefinic silicone compounds, decreases the concentration of IBTMS (or ATMS). These effects can lead to a low rate of the transformation of PIB termini to isobutenyl (allyl) chain ends by IBTMS (ATMS).

It was expected that combination of BCl_3 and TiCl_4 coinitiators would lead not only to controlled polymerization of isobutylene as recently demonstrated^{37,38}, but also to efficient end-quenching by IBTMS, as indicated in Scheme 1. Conditions, yields of isobutenylation (\bar{F}_n), \bar{M}_n and \bar{M}_w/\bar{M}_n are summarized in Table 1. \bar{F}_n was determined by integration of ^1H n.m.r. signals. ^1H n.m.r. of a partially isobutenylated PIB (sample 4), the structure of the polymer and the identification of the n.m.r. signals are shown in Figure 1. \bar{F}_n was determined by calculating the average of functionalities obtained by comparing integral ratios of B/A, C/A, F/A, B/E, C/E and F/E. As shown in Table 1, isobutenyl endgroups were not detected and PIB with broad MWD and a high



Scheme 1 Isobutenylation of carbocationic species by IBTMS

Table 1 Effect of reaction conditions on the isobutenyl functionality (\bar{F}_n) of PIB obtained by end-quenching living isobutylene polymerization with IBTMS

Sample number	$\frac{[\text{TiCl}_4]}{[I]_0}$	$\frac{[\text{IBTMS}]}{[I]_0}$	Reaction time (min)	\bar{F}_n (%)	\bar{M}_n	\bar{M}_w/\bar{M}_n
1	20.0	2.2	142	0	2250	1.52
2	5.2	2.2	160	19 ± 1	2050	1.17
3	5.2	3.4	54	27 ± 1	1750	1.25
4	5.2	5.6	65	38 ± 2	2000	1.25

Polymerization conditions: $I_0 = 5 \times 10^{-4}$ mol *t*BuDiCumOH, 1.1×10^{-2} mol BCl_3 , 1.8×10^{-2} mol *i*-C₄H₈, 10^{-3} mol DMA, 2.5×10^{-5} mol *Dt*BP, $V = 64$ ml (40/60 v/v CH₂Cl₂/hexane), -78°C

MW tail was formed when relatively high concentrations of TiCl_4 were used (sample 1). However, the ^1H n.m.r. spectrum of this sample indicated that ~60% of the *tert*-chlorine endgroups had been consumed. This finding can be interpreted by assuming that isobutenylation occurs and then the ensuing isobutenyl groups react with the carbocations leading to chain coupling as shown in Scheme 2. This is in agreement with recent findings³⁹ according to which chain coupling is facilitated by the presence of *Dt*BP in TiCl_4 -coinitiated living polymerization of isobutylene. The use of lower concentrations of TiCl_4 and higher concentrations of IBTMS resulted in isobutenyl endgroups and PIB with relatively narrow MWD (samples 2–4) indicating that consumption of the isobutenyl chain ends in the coupling reaction can be suppressed by selecting optimal end-quenching conditions. However, a reaction time of ~1 h was not sufficient to achieve high yields of endfunctionalization with IBTMS in the presence of BCl_3 and TiCl_4 . It is noteworthy that upon isobutenylation with IBTMS there was not any observable signal in the ^1H n.m.r. spectra at 5.15 ppm characteristic for the internal $-\text{CH}=\text{C}(\text{CH}_3)_2$ olefinic endgroup formed as side product in ~3–8% by dehydrochlorination of *tert*-chlorine chain ends with *t*BuOK^{26–28}.

Results obtained at different reaction times are summarized in Table 2. As these data indicate, high yield of isobutenylation can be achieved with prolonged reaction times. After ~6 h reaction time (sample 7) for isobutenylation, complete transformation of the chain ends to the isobutenyl group was detected. However, as the comparison of the g.p.c. traces of samples 5 and 7 in Figure 2 indicates, coupling as side reaction occurs between living PIB chains and isobutenyl-ended polymers leading to duplication and even triplication of molecular weight.

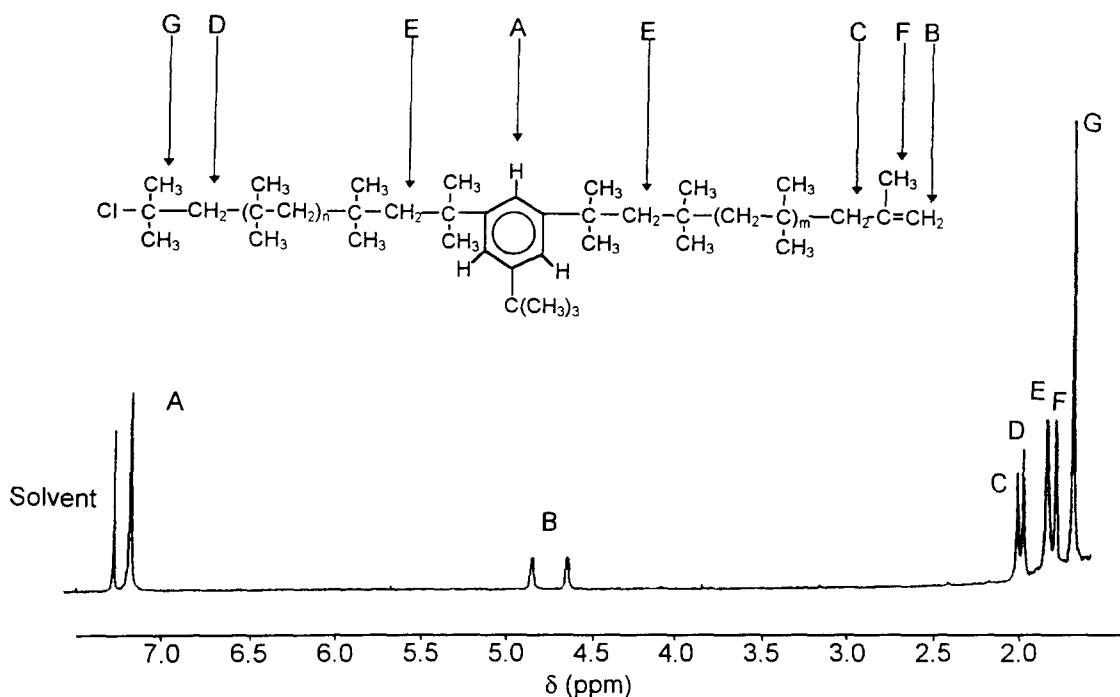
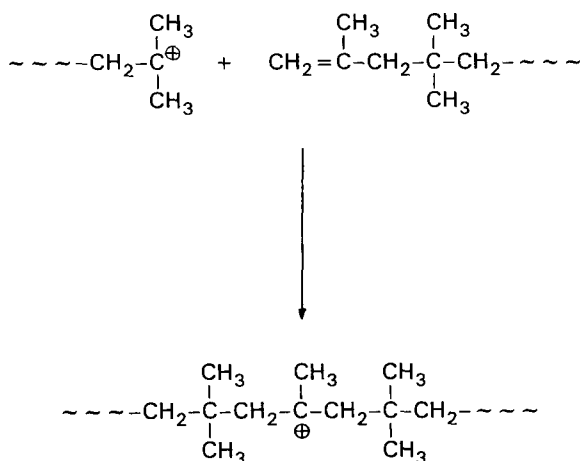


Figure 1 ^1H n.m.r. spectrum of partially isobutenylated PIB (sample 4); solvent: CDCl_3



Scheme 2 Coupling between PIB cation and isobutenyl-ended polymer chain

Table 2 Effect of reaction time on the isobutenyl functionality (\bar{F}_n) of PIB obtained by end-quenching of living isobutylene polymerization with IBTMS

Sample number	$\frac{[\text{IBTMS}]}{[I]_0}$	Reaction time (min)	\bar{F}_n (%)	\bar{M}_n	\bar{M}_w/\bar{M}_n
5	0	0	0	2600	1.15
6	5.4	208	72 ± 3	2800	1.28
7	5.4	351	101 ± 2	2900	1.30
8	5.4	1115 ^a	58 ± 3	3100	1.33

^a Last 720 min at room temperature

Polymerization conditions: $I_0 = 1.27 \times 10^{-3}$ mol *t*BuDiCumOH, 2.5×10^{-2} mol BCl_3 , 6.8×10^{-3} mol TiCl_4 , 6.1×10^{-2} mol *i*-C₄H₈, 2.4×10^{-4} mol DMA, 7.1×10^{-5} mol DiBP, $V_0 = 156$ ml (40/60 v/v $\text{CH}_2\text{Cl}_2/\text{hexane}$), -78°C

Allowing the reaction mixture to warm up to room temperature and extending the reaction time (sample 8) did not help improving isobutenylation, but further consumption of the isobutenyl endgroups was observed.

Allylation with ATMS was also attempted under identical conditions used for samples 5–8 (see Table 2). A reaction time of 90 min led to only 50% allylation indicating the rate reducing effect of BCl_3 in this case as well. However, as shown in Figure 2c the MWD remained monomodal, i.e. chain coupling was absent between allyl-ended PIB and living PIB cations, reflecting probably an unfavourable transformation from a tertiary to a secondary carbocation.

End-functionalization of tert-chlorine-telechelic PIB with IBTMS

End-functionalization of tert-chlorine-telechelic PIB with IBTMS was carried out in $\text{CH}_2\text{Cl}_2/\text{hexanes}$ (40/60 v/v) solvent mixture in the presence of TiCl_4 as described in Experimental. Figure 3 shows the ^1H n.m.r. spectrum of the resulting polymer. This spectrum indicates quantitative end-functionalization and formation of isobutenyl-telechelic PIB by this process. The integration of n.m.r. signals A, B, C, E and F gave average functionality (number of functional groups per chain) $\bar{F}_n = 2.03 \pm 0.06$. It is noteworthy that there is no sign of the ^1H n.m.r. signal at 5.15 ppm characteristic of the *endo* olefinic proton in $-\text{CH}=\text{C}(\text{CH}_3)_2$ endgroup which is usually formed in $\sim 3\text{--}8\%$ of total double bonds by dehydrochlorination of a strong base, such as *t*BuOK^{11,26–29} or CH_3ONa ¹².

As shown in Figure 2d, the g.p.c. trace of this polymer shows that significant chain coupling could not occur under conditions used for end-functionalization with IBTMS. This means that isobutenyl-telechelic PIBs with quantitative end functionality and narrow MWD can be obtained by end-functionalization of tert-chlorine-telechelic PIB with IBTMS in the presence of TiCl_4 . Since side reactions, such as *endo* olefin formation, are absent by this method, isobutenylation with IBTMS provides an improved alternative to quantitative dehydrochlorination of tert-chlorine-ended PIBs by a strong base, e.g. *t*BuOK^{11,26–29} or CH_3ONa ¹². In other words, isobutenylation with IBTMS yields exclusively isobutenyl

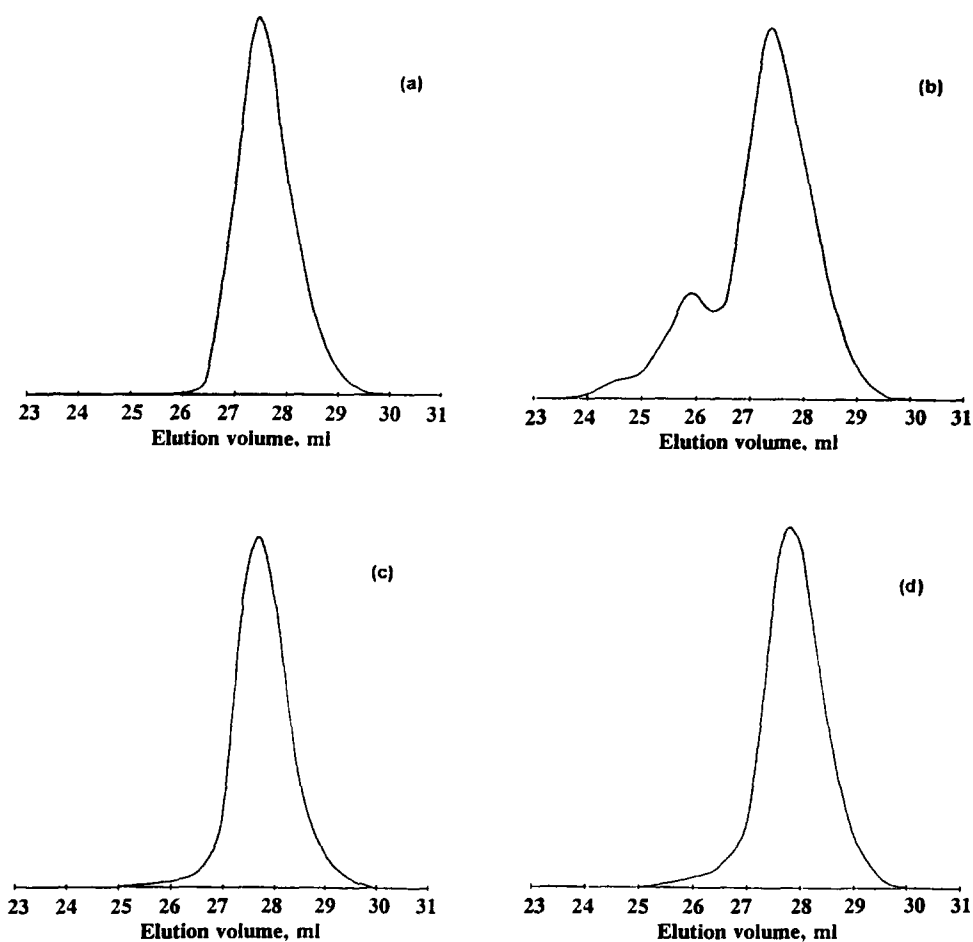


Figure 2 G.p.c. traces of different PIBs: (a) sample 5; (b) sample 7; (c) PIB after reaction of living PIB with ATMS; (d) PIB after end-functionalization of *tert*-chlorine-telechelic PIB with IBTMS (see tables and text for sample identification)

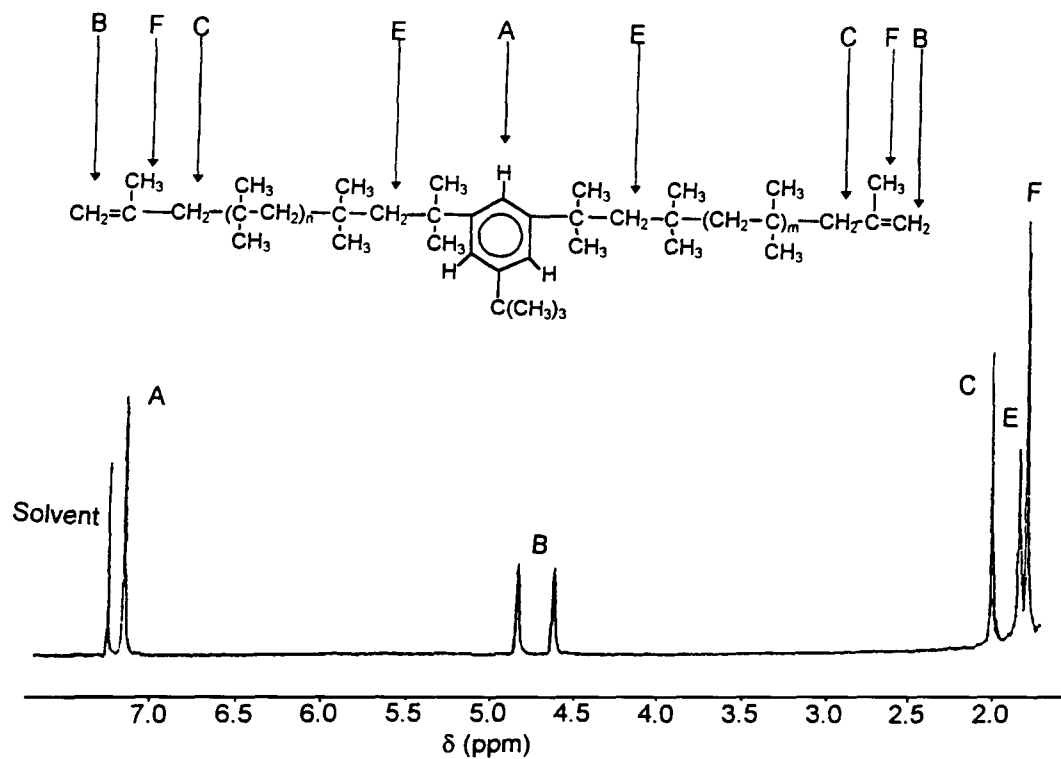


Figure 3 ^1H n.m.r. spectrum of isobutenyl-ended PIB obtained by isobutenylation of *tert*-chlorine-telechelic PIB with IBTMS in the presence of TiCl_4 (see Experimental for details); solvent: CDCl_3

endgroups, and thus leads to exact isobutenyl-telechelic PIBs.

ACKNOWLEDGEMENT

This study was supported by the Danish Materials Technology Development Program, MUP2, and carried out within the framework of the Danish Polymer Centre.

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