New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer Agents (Inifers)
16. Synthesis and Characterization of Polyisobutylenes with Si-Cl and Si-H End-Groups

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Summary
      This paper concerns the synthesis and character-
ization of new Si-Cl and Si-H end-groups containing
polyisobutylenes. The syntheses involved 1) The pre-
paration of polyisobutylenes carrying one or two $-CH_2C-$
$(CH_3)=CH_2$ termini, ii) Hydrosilylation with $H(CH_3)_2-$
$SiCl$, $H(CH_3)SiCl_2$, and $HSiCl_3$, and iii) Reduction of
the Si-Cl groups to yield the corresponding -Si-H ter-
mini. A series of model compounds mimicking the end-
groups have been synthesized and employed for end-group
characterization. These Si-Cl and Si-H containing
mono- and difunctional polyisobutylenes may be useful
intermediates for the preparation of block and graft
copolymers or for the synthesis of various terminal
functional groups.

Introduction
      Polymers containing reactive end-groups are of
interest for block and/or graft copolymer syntheses
(FRENCH 1969; GOBRAN 1964; KENNEDY, SMITH 1980), end-
group derivatizations (BRODY et al. 1958; MORTON, RUBIO
1978; REMPP, LOUCHEUX 1958), and for chain extension
and cross-linking (SAUNDERS, FRISCH 1963; URANECK et al.
1960). The aim of this research was the preparation of
end-group silicon-functionalized polyisobutylenes and
thus to combine the unique physical properties offered
by the rubbery polyisobutylene segment with the versa-
tility and chemical reactivity of the Si-Cl and Si-H
bonds (PLUM, ATHERTON 1973; VAUGHN 1969; WEIBERG,
AMBERGER 1971).

Experimental
      A. Materials and Characterization Methods
      2,4,4-Trimethyl-1-pentene (TMP), 1,2-dimethoxy-
ethene (Aldrich), n-heptane and tetrahydrofuran (THF)
(Fisher Scientific) were freshly distilled over calcium
hydride under nitrogen. Dimethylchlorosilane, methyl-
dichlorosilane, trichlorosilane (Petrarch Systems),
absolute ethanol, chloroplatinic acid (Fisher Scienti-
fic), calcium hydride, and lithium aluminum hydride

(LAH) (Alfa) were used as received. The syntheses of
α-tert-butyl-ω-isobutenyl-polyisobutylene (tBu-PIB-
$CH_2C(CH_3)=CH_2$) and α,ω-di(isobutenyl)polyisobutylene
($CH_2=C(CH_3)CH_2$-PIB-$CH_2C(CH_3)=CH_2$) have been described
(KENNEDY et al. 1979).

^{1}H NMR spectra were obtained on a Varian T-60 in-
strument. Infrared spectra were recorded on a Perkin-
Elmer 521 Spectrophotometer.

B. Syntheses of Model Compounds
2,4,4-Trimethylpentyldimethylchlorosilane (tBu-
$CH_2C(CH_3)_2Si(CH_3)_2Cl$) (1), 2,4,4-Trimethylpentylmeth-
yldichlorosilane (tBuCH$_2$C(CH$_3$)$_2$Si(CH$_3$)Cl$_2$) (2), and
2,4,4-Trimethylpentyltrichlorosilane (tBuCH$_2$C(CH$_3$)-
CH$_2$SiCl$_3$) (3). A 250 ml three-neck flask equipped
with a condenser, dropping funnel, magnetic stirrer,
and gas inlet tube, was charged with 100 ml dry n-hep-
tane and 15 ml (0.095 mole) 2,4,4-trimethyl-1-pentene.
The charge was refluxed and while dry nitrogen was bled
through the flask 0.01 ml chloroplatinic acid solution
(chloroplatinic acid: 1,2-dimethoxyethane : ethanol =
1 : 9 : 1)(CHUANG 1975) was added; then 25 ml (0.225
mole) dimethylchlorosilane was added dropwise over a
period of 30 min. Periodically an aliquot was removed
and examined by ^{1}H NMR. After the olefin has been con-
sumed ($\sim$20 hrs) the mixture was cooled to room temper-
ature. The solution of the crude product was concen-
trated by distillation, and subsequently vacuum dis-
tilled to yield 16.8 g (86%) of 1: Bp. 83-4°C,5 mm.
By the same procedure, 40 ml (0.25 mole) TMP and 35 ml
(0.34 mole) methyldichlorosilane yielded 52.3 g (92%)
of 2: Bp. 57-9°C, 1 mm. Similarly, 40 ml (0.25 mole)
TMP and 28 ml (0.28 mole) trichlorosilane yielded 59.
5g (96%) of 3: Bp. 70°C, 3.2 mm.
2,4,4-Trimethylpentyldimethylsilane (tBuCH$_2$C(CH$_3$)-
CH$_2$Si(CH$_3$)$_2$H) (4), 2,4,4-Trimethylpentylmethylsilane
(tBuCH$_2$C(CH$_3$)CH$_2$Si(CH$_3$)H$_2$) (5), and 2,4,4-Trimethyl-
pentylsilane (tBuCH$_2$C(CH$_3$)CH$_2$SiH$_3$) (6). A 250 ml three-
neck flask equipped with condenser, magnetic stirrer,
dropping funnel, and nitrogen inlet tube was charged
with 3.3 g (0.087 mole) LAH suspension in 50 ml anhy-
drous THF. Then 15 ml (0.06 mole) 1 was added dropwise
into the stirred suspension and the mixture was stirred
for an additional hour at room temperature. The mix-
ture was poured over a stirred mixture of 50 ml ether,
100 g crushed ice, and 100 ml ice-cold 0.5 N HCl (when
necessary more ice was added to keep the mixture cold).
The layers were separated and the organic layer was
concentrated by distillation over calcium hydride.
Subsequent vacuum distillation gave 7.9 g (77%) of 4:
Bp. 43°C, 10.5 mm; IR (CCl$_4$)ν_{Si-H} 2110 cm^{-1}; ^{1}H NMR
(CCl$_4$) δ 0.1 (methyl, d, 6H),0.9 (methyl, s, 12H),
1.0-1.3 (methylene and methine, m, 5H), 3.85 (silyl, m,

1H). Following the same procedure, 20 ml (0.09 mole) 2 and 7.5 g (0.02 mole) LAH yielded 11.8 g (83%) of 5: Bp. 43-4°C, 14 mm; IR (CCl₄)ν_{Si-H} 2120 cm^{-1}, ^{1}H NMR (CCl₄) δ 0.1 (methyl, t, 3H), 0.9 (methyl, s, 12H), 1.0-1.3 (methylene and methine, m 5H), 3.7 (silyl, m, 2H). Similarly, 20 ml (0.08 mole) 3 and 10 g (0.26 mole) LAH yielded 8.8 g (76%) of 6: Bp. 52°C, 16 mm, IR (CCl₄)ν_{Si-H} 2140 cm^{-1}; ^{1}H NMR (CCl₄) δ 0.9 (methyl, s, 12H), 1.0-1.3 (methylene and methine, m, 5H), 3.5 (silyl, t, 3H).

C. Polymer End-Group Derivatization

α-tert-Butyl-ω-dimethylchlorosilylpolyisobutylene (PIB-SiCl) (7) and α,ω-Di(dimethylchlorosilyl)polyisobutylene (ClSi-PIB-SiCl) (8).

Using the procedure described for the synthesis of 1, 5 g (8.3 mmole) tBu-PIB-CH₂C(CH₃)=CH₂ ($\overline{M}_n \sim 550$), 100 ml dry n-heptane, 15 ml (0.134 mole) dimethylchlorosilane and 0.05 ml chloroplatinic acid solution were employed to synthesize 7. Since the Si-Cl bond is very moisture sensitive, the purification of 7 is very difficult; thus after solvent evaporation the product was used without further purification. Similarly, 3 g (1 mmole) CH₂=C(CH₃)CH₂-PIB-CH₂C(CH₃)=CH₂ ($\overline{M}_n \sim 3,000$), 100 ml dry n-heptane, 3.0 ml (27 mmole) dimethylchlorosilane, and 0.05 ml chloroplatinic acid solution were used to obtain 8.

α-tert-Butyl-ω-dimethylsilylpolyisobutylene (PIB-SiH) (9) and α,ω-Di(dimethylsilyl)polyisobutylene (HSi-PIB-SiH) (10).

Using the procedure described for the synthesis of 4, a concentrated solution containing 3 g (∿ 5 mmole) 7 ($\overline{M}_n \sim 650$) and 2 g LAH suspension in 50 ml THF were employed to obtain 9. After the reaction, the mixture was concentrated by vacuum evaporation and 100 ml dry n-heptane was added to precipitate the excess LAH. Subsequently, the solution was filtered and poured slowly under stirring over a mixture of 100 ml ice-cold 0.5 N HCl and 100 g crushed ice. The solvent was evaporated and the product 9 was kept in vacuo at room temperature overnight. Similarly, a concentrated solution containing ∿ 2 g (0.65 mmole) 8, ($\overline{M}_n \sim 3,100$) and 2 g LAH suspension in 50 ml THF was used to obtain 10.

Results and Discussion

The hydrosilylation (WEIBERG, AMBERGER 1971; VOROKOV 1977) of polyisobutylenes with -CH₂C(CH₃)=CH₂ end-groups was simulated by hydrosilylating TMP with dimethylchlorosilane, methyldichlorosilane, and trichlorosilane. The yields of 1, 2, and 3 were quantitative as indicated by ^{1}H NMR analysis. These model compounds were then quantitatively reduced with LAH to

4, 5, and 6, and used as standards for end-group characterization.

PIB-SiCl and ClSi-PIB-SiCl were obtained by hy-drosilylating tBu-PIBCH$_2$C(CH$_3$)=CH$_2$ and CH$_2$=C(CH$_3$)CH$_2$-PIB-CH$_2$C(CH$_3$)=CH$_2$ with dimethylchlorosilane. Since the Si-Cl bond is highly moisture sensitive, it is extreme-ly difficult to purify PIB-SiCl and ClSi-PIB-SiCl. Thus direct functionality analysis has not been per-formed, and the concentrated solutions of 7 and 8 were used without purification. Indirect evidence, however, indicates quantitative conversion, i.e., characteriza-tion of PIB-SiH (9) and HSi-PIB-SiH (10), obtained by reduction from 7 and 8.

The syntheses of PIB-SiH and HSi-PIB-SiH have been carried out by the reduction of PIB-SiCl and ClSi-PIB-SiCl with LAH. Figure 1 shows the ^{1}H NMR spectrum of HSi-PIB-SiH. The olefinic proton resonances at 4.58 and 4.68 ppm of CH$_2$=C(CH$_3$)CH$_2$-PIB-CH$_2$C(CH$_3$)=CH$_2$ (KENNEDY et al. 1979) have disappeared, and new peaks that appeared at 3.9-4.3 ppm and 0.0-0.2 ppm were as-signed to the -Si(C$\underline{H}_3$)$_2$H and Si(CH$_3$)$_2$$\underline{H}$ protons, re-spectively. These assignments were confirmed by com-parison with the ^{1}H NMR spectrum of 4. Significantly, integration of aromatic protons/Si-$\overline{H}$ yields 2.0±0.1 which is evidence for quantitative hydrosilylation in the synthesis of 8 and thence for the quantitative re-duction of 8 to 10.

Further evidence for the quantitative conversion of the 1-olefin end-group to dimethylsilyl end-groups was provided by qualitative and quantitative IR anal-ysis of HSi-PIB-SiH. As shown by Figure 2 the charac-teristic bands of the terminal 1-olefins at 3060, 1780, 1640, and 890 cm^{-1} disappeared after hydrosilylation and a new band characteristic of the Si-H end-groups appeared at 2110 cm^{-1} (SMITH 1974). Quantitative IR analysis of the Si-H end-group gave a functionality of 1.9$_3$±0.1. This analysis was performed by the use of a calibration curve obtained with model 1 (Figure 3) in conjunction with $\overline{M}_n$ of Sample 10 ($\overline{M}_n$= 3,100 by GPC).

REFERENCES

BRODY, H.H., RICHARDS, D.H., and SZWARC, M., Chem. Ind. (London), 45, 1473 (1958).
CHUANG, V.T., U.S. Patent, 3,925,434 (Dec. 9, 1975) to Union Carbide.
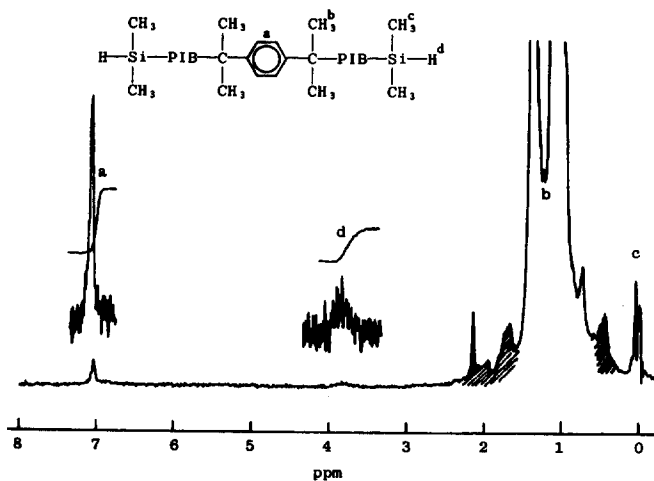FRENCH, D.M., Rubber Chem. Technol., 42, 71 (1969).

Figure 1. H^1 NMR Spectrum of α,ω-Di(dimethylsilyl)-
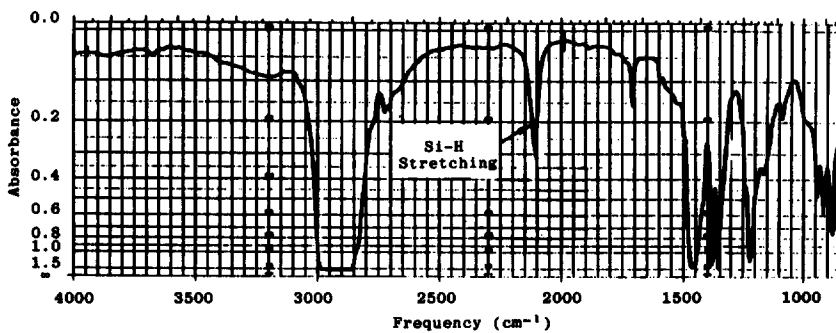polyisobutylene (<u>10</u>)

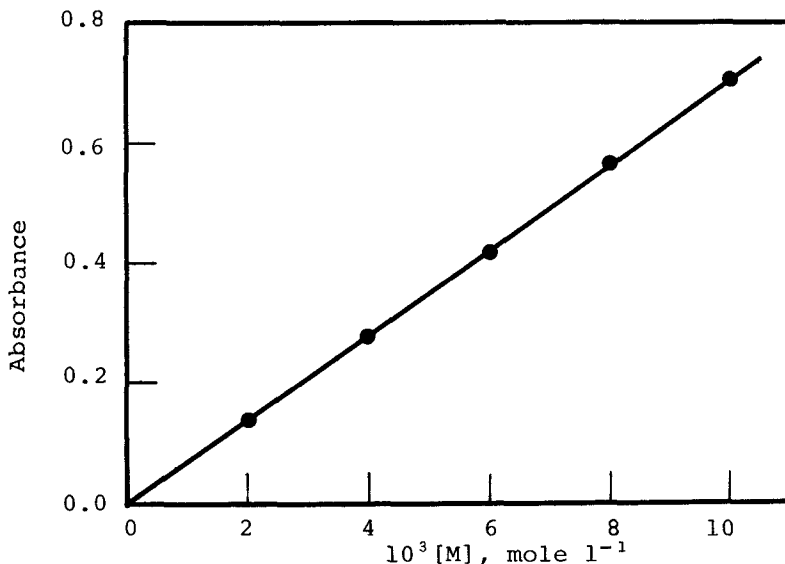Figure 2. IR Spectrum of α,ω-Di(Dimethylsilyl)-
polyisobutylene (<u>10</u>)

Figure 3.   IR Calibration Curve of 2,4,4-Trimethyl-
pentyldimethylsilane (4) at 2110 cm^{-1} in
CCl$_4$

GOBRAN, R.H., "Chemical Reactions of Polymers",
FETTES, E.M., Ed., Interscience, New York, 1964, p. 295.
KENNEDY, J.P., and SMITH, R.A.: J. Polym. Sci., Polym.
Chem. Ed., 18, 1539 (1980).
KENNEDY, J.P., CHANG, V.S.C., SMITH, R.A., and IVAN, B.,
Polymer Bulletin, 1, 535 (1979).
MORTON, M., and RUBIO, D.C., Plastic and Rubber: Mate-
rials and Applications, 3, 139 (1978).
PLUM, J.B., and ATHERTON, J.H., "Copolymers Containing
Polysiloxane Blocks" in "Block Copolymers", ALLPORT, D.
C., and JANES, W.H., Ed., John Wiley, New York, 1973,
p. 305.
REMPP, P., and LOUCHEUX, M.H., Bull. Soc. Chim. France,
1497 (1958).
SAUNDERS, J.H., and FRISCH, K.C., "Polyurethanes:
Chemistry and Technology", Interscience, New York, 1963.
SMITH, A.L., "Analysis of Silicones", John Wiley, New
York, 1974, p.247.
URANECK, C.A., HSIEH, H.L., and BUCK, O.G., J. Polym.
Sci., 46, 535 (1960).
VAUGHN, H.A., Polymer Letters, 7, 569 (1969).
VOROKOV, M.G., "Hydrosilylation. Recent Achievements"
in J. Organometal. Chem. Library 5, SEYFERTH, D., Ed.,
Elsevier Publishing, 1977, p. 1.
WEIBERG, E., and AMBERGER, E., "Hydrides of the
Elements of Main Groups I-IV", Elsevier Publishing,
1971. p. 513.