

Initiation

New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer Agents (INIFERS)

40. Telechelic Polyisobutylenes by Sterically Hindered Binifers

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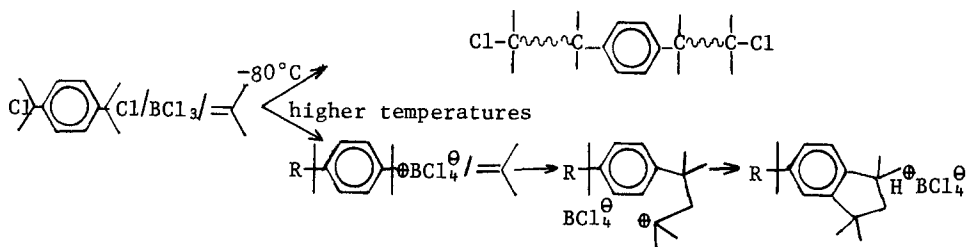
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SUMMARY

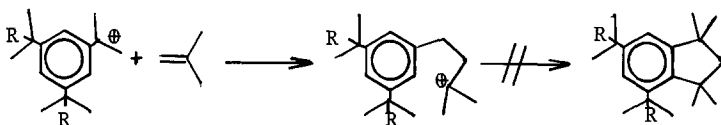
The synthesis of α,ω -di-tert-chloropolyisobutylenes (chlorine-telechelic PIB's) have been accomplished at -30°C by the use of "sterically hindered inifers". A suitable sterically hindered binifer is 1,3-di(2-chloro-2-propyl)-5-tert-butylbenzene, m-tBuDCC, i.e., a binifer in which the bulky tert-butyl group prevents undesirable intramolecular alkylation with concomitant proton elimination. Conventional binifers i.e., 1,4-di(2-chloro-2-propyl)benzene (p-dicumyl chloride, pDCC) give rise to this unacceptable side reaction unless the inifer process is carried out at -80° . The use of m-tBuDCC leads to satisfactory telechelic PIB's with number average end functionalities (\bar{F}_n) of 2.0 ± 0.1 . The \bar{F}_n and \bar{M}_n of the products are unaffected by temperature in the -30 to -80°C range. In the absence of the bulky tert-butyl group in the inifer, i.e., with 1,3-di(2-chloro-2-propyl)benzene, mDCC, severe indanyl ring formation occurs.

INTRODUCTION

The synthesis of linear and three-arm star telechelic PIB's, by the inifer technique has recently been discovered^{1,2} and some of its fundamentals and ramifications described in this series of publications (for the last paper of this series see ref. 3). Linear α,ω -di-tert-chloropolyisobutylenes can be readily prepared by the pDCC/ BCl_3 /isobutylene system at -80°C , however, at higher temperatures unacceptable indanyl ring formation (intramolecular cyclization) may occur:

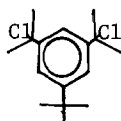


where $\text{R}=\text{Cl}$ or PIB chain. If $\text{R}=\text{Cl}$, a second indanyl ring may also form^{4,5}. Indanyl ring formation is accompanied by H^+ expulsion and (just as chain transfer to monomer) leads to "sterile" $-\text{CH}_3$ groups detrimental for the synthesis of end reactive prepolymers. In contrast, indanyl ring formation is absent during the synthesis of three-arm star telechelic PIB's by the use of trinifers⁶, most likely because intramolecular alkylation cannot occur in this hindered system:



where R = Cl or PIB.

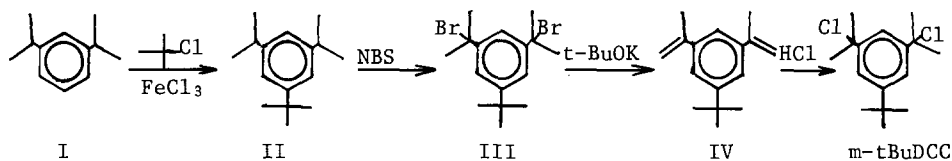
In line with these observations we postulated that linear telechelic PIB's devoid of indanyl structures could be synthesized by the use of "sterically hindered" binifers, i.e., bifunctional inifers carrying a tert-butyl group, e.g., *m*-*t*-BuDCC:



EXPERIMENTAL

A. Syntheses

The overall synthesis is shown by the following equation:



tert-Butyl chloride (20 ml, 0.18 moles) was added dropwise to a mixture of I (100ml) and FeCl_3 (13g, 0.08 moles) at 0°C . After the evolution of HCl the mixture was washed with water, dried with CaCl_2 , and distilled under vacuum. According to ^1H NMR spectroscopy the product was pure II; δ (ppm) = 6.85 (aromatic, s, 3H), 2.8 (methine, m, 24), 1.25(methyl, s, 12H) and 1.15(methyl, s, 9H).

III was prepared by adding II (22g, 0.10 moles) to a stirred solution of *N*-bromosuccinimide (39g, 0.22 moles) and benzoyl peroxide (5g, 0.02 moles) in CCl_4 (200 ml). After reaching the boiling point of the solution the NBS rises to the top (~ 1 min). The system was cooled with ice, filtered, and after evaporating the solvent (rotovap) the product was recrystallized from *n*-hexane (Mp = $75-76^\circ\text{C}$). ^1H NMR spectroscopy showed essentially pure III; δ (ppm) = 7.35(aromatic, s, 3H), 2.15(methyl, s, 12H), 1.35(methyl, s, 9H).

IV was prepared by dehydrobromination of III with *t*-BuOK. Thus a solution of *t*-BuOK (25g, 0.22 moles) in THF (250 ml) was added dropwise to a solution of III (18.8g, 0.05 moles) in THF (250 ml) over a period of 30 min. at 0°C . Then the mixture was warmed slowly to room temperature. After 5 hours of stirring *n*-hexane (500 ml) was added. The product was washed with water, dried with CaCl_2 and vacuum distilled. According to ^1H NMR spectroscopy the colorless liquid appeared to be essentially pure IV, δ (ppm) = 7.15 (aromatic, s, 3H), 5.14-4.95 (vinyl, d, 4H), 2.15(methyl, s, 6H), 1.35 (methyl, s, 9H).

The *m*-*t*-BuDCC was obtained by hydrochlorination of IV. Thus HCl was bubbled through a solution of IV (10g, 0.05 moles) in CH_2Cl_2 (100 ml) at

0°C for several hours. The solvent was removed and the product was re-crystallized from *n*-hexane (Mp of colorless crystals = 66-68°C). ¹H NMR δ(ppm) = 7.6 (aromatic, s, 3H), 205 (methyl, s, 12H), 1.4 (methyl, s, 9H). ¹³C NMR: δ(ppm) = 150.87 (aromatic, substituted), 145.69 (aromatic, substituted), 121.78 (aromatic), 119.82 (aromatic), 69.98 (aliphatic, quaternary), 35.43 (aliphatic, quaternary), 34.38 (methyl), 31.35 (methyl).

The synthesis of the 1,3-di(3-chloro-1,1,3-trimethylbutyl)-5-tert-butylbenzene model compound was carried out by the same technique used for the preparation of 1,4-di(3-chloro-1,1,3-trimethylbutyl)benzene⁵. The product obtained was a colorless liquid. ¹H NMR: δ(ppm) = 7.1 (aromatic, s, 3H), 2.35 (methylene, s, 4H), 1.55 (methyl, s, 12H), 1.40 (methyl, s, 9H), 1.35 (methyl, s, 12H).

B. Polymerization and Characterization

The polymerization of isobutylene with *m*-tBuDCC was carried out by the same technique used with the conventional binifer, i.e., pDCC^{4,6}.

¹H NMR spectra were obtained on a Varian HR-300 and Varian T-60 NMR instrument, and ¹³C NMR spectra on a Varian CFT-20 instrument. Melting points were determined by a Laboratory Devices Melt-Temp. instrument. Molecular weights were determined by GPC; the instrument and methodology have been described⁴⁻⁸.

RESULTS AND DISCUSSION

A. Polymerization of Isobutylene with *m*-tBuDCC

Earlier investigations showed that isobutylene polymerizations have to be carried out at low temperatures (<-50°C), particularly in the presence of high binifer (pDCC) and low isobutylene concentrations, to avoid indanyl ring formation⁴. Thus isobutylene was polymerized by the *m*-tBuDCC/BCl₃ system using CH₃Cl or CH₂Cl₂ or these solvents in combination with 20% *n*-C₆H₁₄, in the range from -20 to -80°C. The desired \bar{M}_n range was from 1500 to 5000g/mole to facilitate end group determination and terminal indanyl structure analysis.

¹H NMR spectra of PIB's prepared even at relatively high temperatures (-30°C) and in polar solvents⁷ showed the absence of resonances at 6.95 and 6.75 ppm^{4,5} i.e., absence of mono- and di-indanyl structures, respectively. Figure 1 shows a typical ¹H NMR spectrum together with structure assignments¹⁰. The resonances at 2.34 and 1.59 ppm were assigned on the basis of the ¹H NMR spectrum of the model compound shown in Figure 2. The latter spectrum shows a resonance at 2.05 ppm that is due to the unreacted binifer. The resonances at 0.88 (11) and 1.29 (10) ppm are due to *n*-hexane impurities. The resonance at 0.93 (12) ppm is a spinning band and its symmetrical signal is masked by the resonance at 1.31 ppm.

Figure 3 shows the ¹³C NMR spectrum of the same PIB sample together with assignments. The resonances were assigned from information obtained from ¹³C NMR spectra recorded under off-resonance decoupling conditions. Signals characteristic of indanyl end groups⁵ are absent.

\bar{M}_n values have been obtained from the ratio of end group concentration (¹H NMR) and molecular weight (\bar{M}_n by GPC). The ¹H NMR method involves the quantitative dehydrochlorination of the -CH₂C(CH₃)₂Cl terminus and integration of the -C=CH₂ protons (aromatic protons internal standard). Figure 4 shows a representative spectrum. The resonances at 4.7 and 4.9 ppm are due to the terminal vinyl protons, whereas that at 4.4 ppm is related

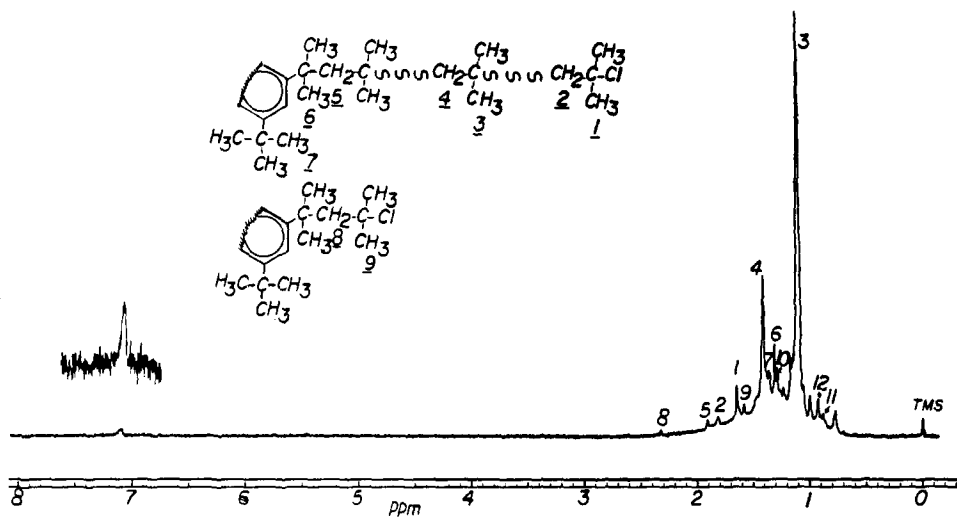


Figure 1. ^1H NMR Spectrum of the Product Obtained by the m - t BuDCC/ BCl_3 /isobutylene/ CH_3Cl / -50°C System ($\bar{M}_n = 2200$)

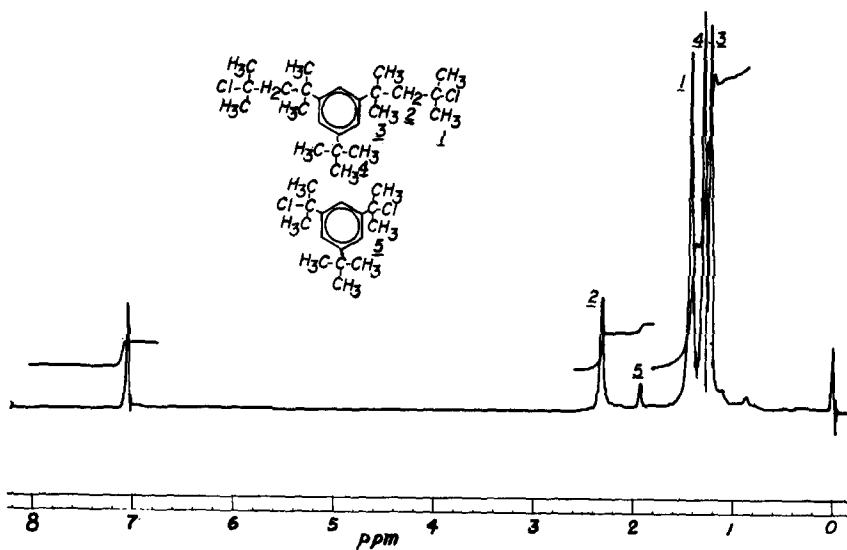


Figure 2. ^1H NMR Spectrum of the Model Compound 1,3-di(3-chloro-1,1,3-trimethylbutyl)-5-tert-butylbenzene

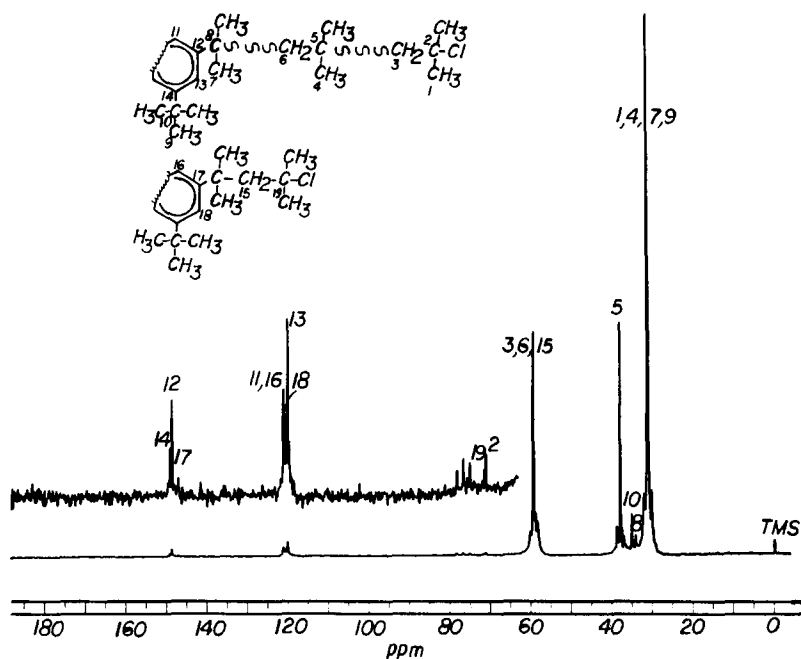


Figure 3. ^{13}C NMR Spectrum of the Product Obtained by the $m\text{-tBuDCC}/\text{BCl}_3/\text{isobutylene}/\text{CH}_3\text{Cl}/-50^\circ\text{C}$ System

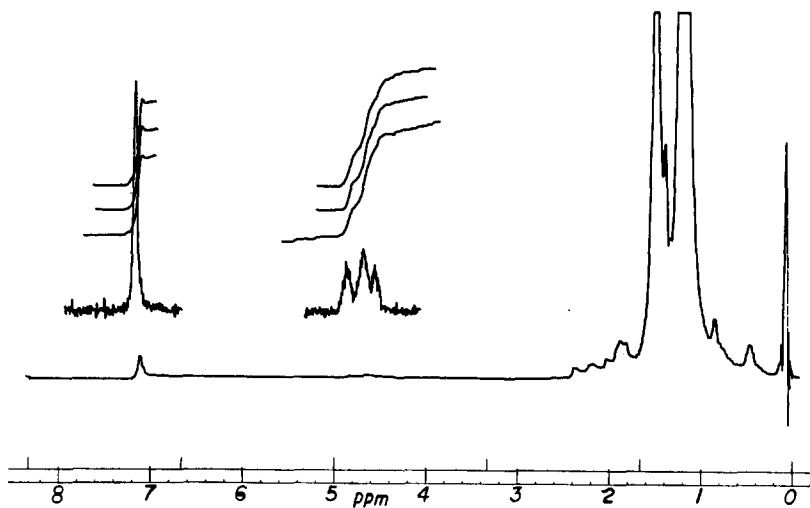


Figure 4. ^1H NMR Spectrum of Dehydrochlorinated PIB Obtained in the $m\text{-tBuDCC}/\text{BCl}_3/\text{isobutylene}/\text{CH}_2\text{Cl}_2\text{-nC}_6\text{H}_{14}$ (5/1 v/v)/ -20°C System ($M_n = 1600$, $M_w/M_n = 2.5$)

to the vinyl protons when only one isobutylene unit is attached to the inifer residue. These experiments follow those made by Tessier and Maréchal⁹. Table I shows $\bar{F}_n = 2.0 \pm 0.1$ is independent of temperature.

The molecular weights obtained by the *m-t*BuDCC/ BCl_3 system are also unaffected by temperature (cf. Table I).

\bar{M}_w/\bar{M}_n values are somewhat higher than the theoretical value of 1.5^{10} which may be due to some low molecular weight species, perhaps to those carrying only one isobutylene unit attached to the inifer residue, as shown by the structures in Figures 1 and 3.

TABLE I
Molecular Weights and Number Average Degrees of End Groups (\bar{F}_n)
of PIB's Obtained by the *m-t*BuDCC/ BCl_3 System

Temperature °C	\bar{M}_n g/mole	\bar{M}_w	\bar{M}_w/\bar{M}_n	\bar{F}_n	Conversion %
-30	1700	3900	2.29	1.98	68.9
-30	2100	4200	2.00	-	-
-40	1800	3500	1.94	1.95	71.5
-50	2300	5300	2.30	2.04	72.7
-70	2200	4900	2.23	1.97	72.5
-80	2200	4300	1.95	1.97	73.0

[IB] = 0.3 M, [*m-t*BuDCC] = 6.72×10^{-3} , [BCl_3] = 3.4×10^{-2} M, CH_3Cl , 5 min.

B. Polymerization with mDCC

To prove that the bulky *t*-Bu substituent in *m-t*BuDCC in fact prevents intramolecular alkylation experiments have been carried out with mDCC i.e., a binifer identical to *m-t*BuDCC except for the absence of the *t*-Bu substituent. The ^1H NMR spectrum of a PIB obtained in a representative experiment using mDCC is shown in Figure 6. The resonance at 6.75 ppm indicates that a significant amount of indanyl ring formation has occurred^{4,5}.

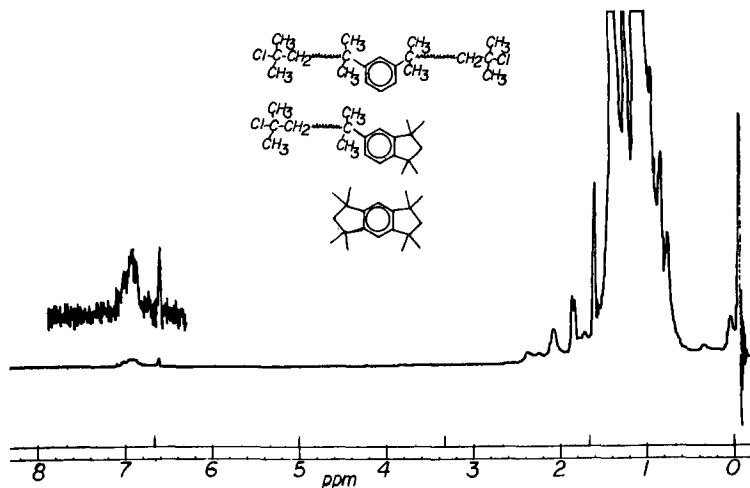
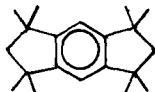


Figure 6. ^1H NMR Spectrum of the Product Obtained by the mDCC/ BCl_3 /isobutylene/ CH_3Cl /-40°C System

Visual inspection of the product showed the presence of white needles characteristic of 1,1,3,3,5,5,7,7-octamethyl-s-hydrindacene⁵:



Following this observation an experiment was carried out with mDCC and 2 moles of isobutylene (BCl_3 and $\text{CH}_2\text{Cl}_2/\text{n-C}_6\text{H}_{14}/1$) at -40°C to prepare 1,1,3,3,5,5,7,7-octamethyl-s-hydrindacene. These investigations also yielded white needles, and structure studies including ^1H NMR and ^{13}C NMR as well as mass spectroscopy indicated that the crystals obtained by earlier workers using pDCC⁵ were identical to these.

ACKNOWLEDGEMENT

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