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

12. Synthesis of New Model Compounds for Cycloalkylation Studies and ^{13}C NMR Characterization of Polyisobutylene

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Summary

Three new symmetrical alkylaromatic sturctures p-bis(3-chloro-1,1,3-trimethylbutyl)benzene (I), p-bis(1,1,3-trimethyl-3-butenyl)benzene (II), and 1,1,3,3,5,5,7,7-octamethyl-s-hydrindacene (III) have been synthesized. These new model compounds were needed to study the mechanism of intramolecular cycloalkylation (indane-skeleton formation) during the preparation of telechelic polyisobutylenes by the inifer technique. The ^{13}C NMR spectrum of polyisobutylene obtained by the p-dicumyl chloride/BCl$_3$ inifer system has been analyzed and the resonances identified.

Introduction

In the course of our fundamental investigations on the mechanism of carbocationic olefin polymerization leading to telechelic products (KENNEDY et al. 1979; KENNEDY, SMITH 1980; IVAN et al. (1980) need arose for the synthesis of three new highly symmetrical alkylaromatic sturctures: p-bis(3,chloro-1,1,3-trimethylbutyl)benzene (I), p-bis(1,1,3-trimethyl-3-butenyl)benzene (II), and 1,1,3,3,5,5,7,7-octamethyl-s-hydrindacene (III). The synthesis principle is outlined in Scheme I. This communication concerns convenient syntheses of these three new model compounds needed in our investigation on the mechanism of intramolecular cycloalkylation (indane-skeleton formation) during the preparation of telechelic polyisobutylenes.

Results and Discussion

As discussed in our previous publication (CHANG et al. 1980) concerning the synthesis of linear telechelic polyisobutylenes, internal cycloalkylation (i.e., indane-skeleton formation) may occur at the very beginning of the chain:

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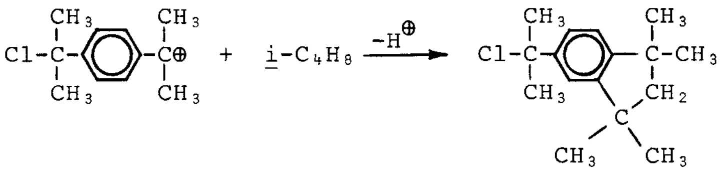
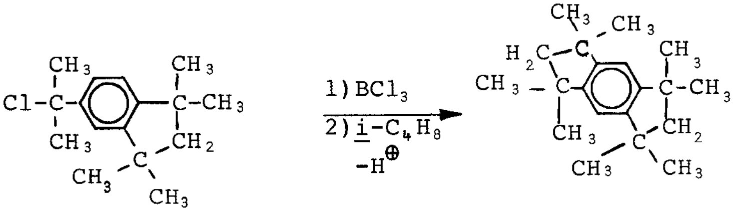


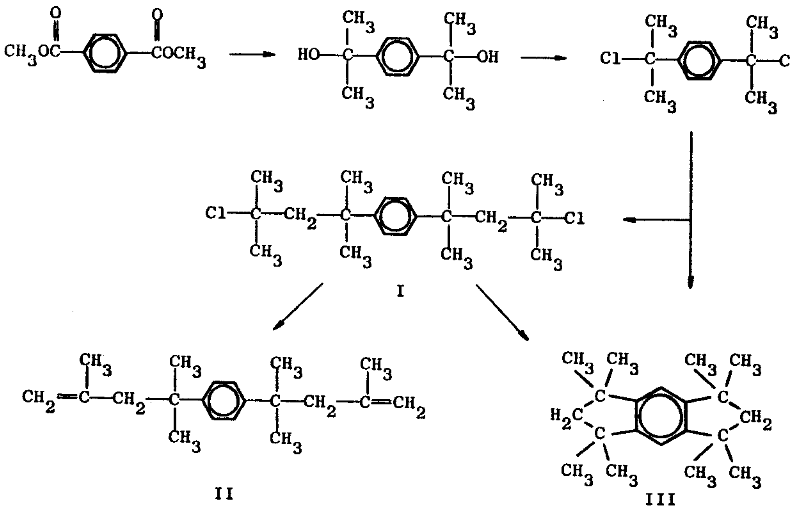
Under certain conditions i.e., low isobutylene concentration, high temperature, even a second indane ring may arise:



These reactions are completely unacceptable if the aim is perfect bifunctionality ($\bar{F}_n = 2.0$), Synthetic conditions have been found under which these very undesirable side-reactions can be avoided (CHANG et al. 1980). Model compounds containing one or two condensed indane-skeletons helped quantifying ^1H NMR spectra in these studies.

Scheme I outlines conversions leading to model compounds I, II and III whose structural similarity

Scheme I. Synthesis of Model Compounds I, II, and III



with the undesirable by-product (III) and desirable telechelic chlorides (I) and olefins (II) were of great help in earlier investigations. Thus I was obtained by adding stoichiometric quantities of isobutylene to p-dicumyl chloride (p-bis(1-chloro-1-methylethyl)benzene in the presence of BCl_3 in a 1:1 mixture of $CH_2Cl_2/n\text{-}C_6H_{14}$ at -40° and II was obtained from I by dehydrochlorination with t-BuOK in refluxing THF. Only the exo-olefin was obtained (BROWN, MORITANI 1956). Conversion was quantitative. Finally, III was obtained either by adding a stoichiometric quantity of isobutylene to p-dicumyl chloride in the presence of BCl_3 in pure CH_2Cl_2 at 40°C or by storing the reaction liquor obtained in the synthesis of I at room temperature for 3 days. The ^1H and ^{13}C NMR spectra of the various model compounds are shown in Figures 1 and 2, respectively.

According to these results cycloalkylation of I proceeds rapidly even at very low temperatures in polar CH_2Cl_2 medium, whereas the use of higher temperatures are required in relatively nonpolar solvent mixtures. Evidently the rate of indane formation is strongly reduced in nonpolar media. The definition of this solvent polarity/temperature effect on the intramolecular cycloalkylation of I was of greatest help in guiding the selection of reaction conditions for the preparation of telechelic polyisobutylenes (KENNEDY, SMITH 1980; KENNEDY et al. 1979; IVAN et al. 1980), syntheses in which indane formation is completely unacceptable (BALDWIN et al. 1969; IVAN, KENNEDY 1980).

In the course of this work we have also prepared low molecular weight polyisobutylenes (PIB) by the use of the p-dicumyl chloride/BCl_3 inifer system for ^{13}C NMR characterization. Figure 3 shows the ^{13}C NMR spectrum of a PIB obtained under conditions conducive for indane end group formation i.e., relatively low monomer concentration, high temperature and polar solvent, suitable for analysis. The resonances have been assigned on the basis of information obtained from the ^{13}C NMR spectra of model compounds I and III. According to this spectrum the presence of indane end group is indicated by resonances a' and b' at 120 and 123 ppm, and by the complex shoulder at ∿150 ppm. We believe this technique is superior to the ^1H NMR method published earlier (CHANG et al. 1980) for the detection of indane end groups in PIB's synthesized by the inifer system.

Experimental

^1H NMR spectra were obtained on a Varian T-60 instrument. ^{13}C NMR spectra were obtained on a Varian CFT-20 instrument. Infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer. Melting points

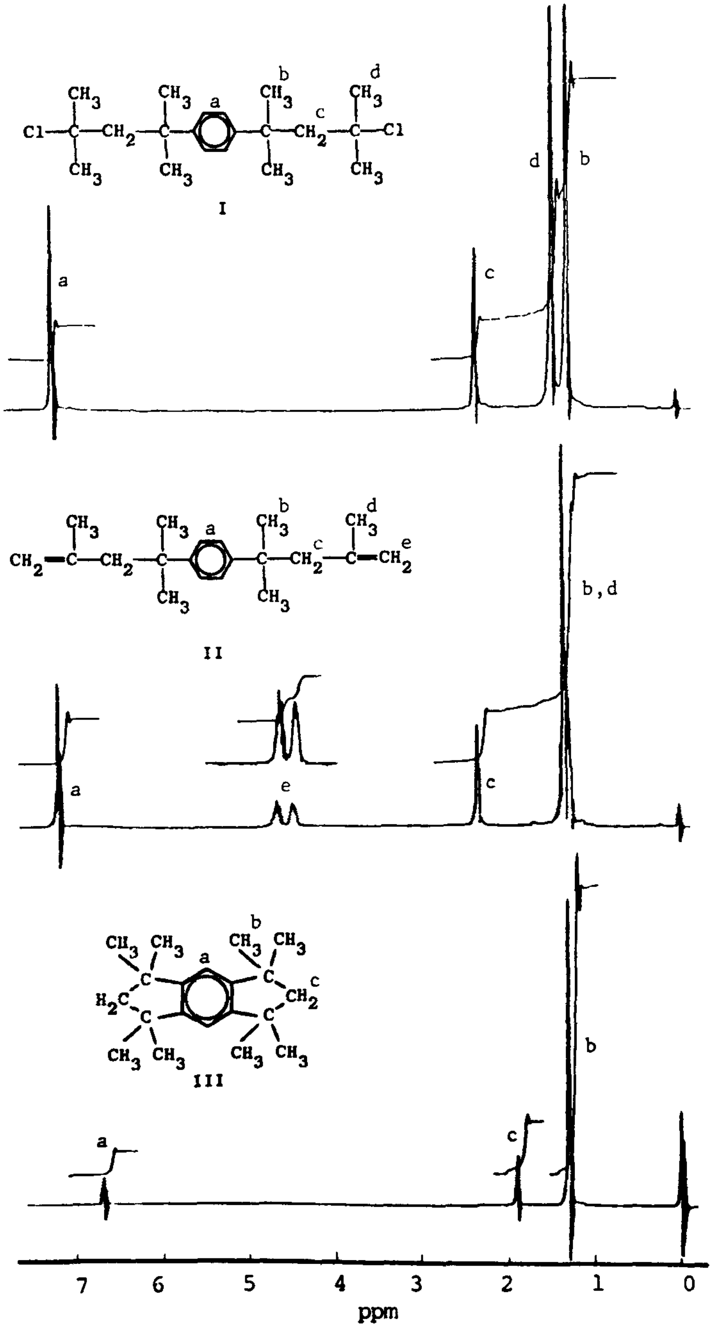


Figure 1. ^{1}H NMR Spectra of Model Compounds I, II and III.

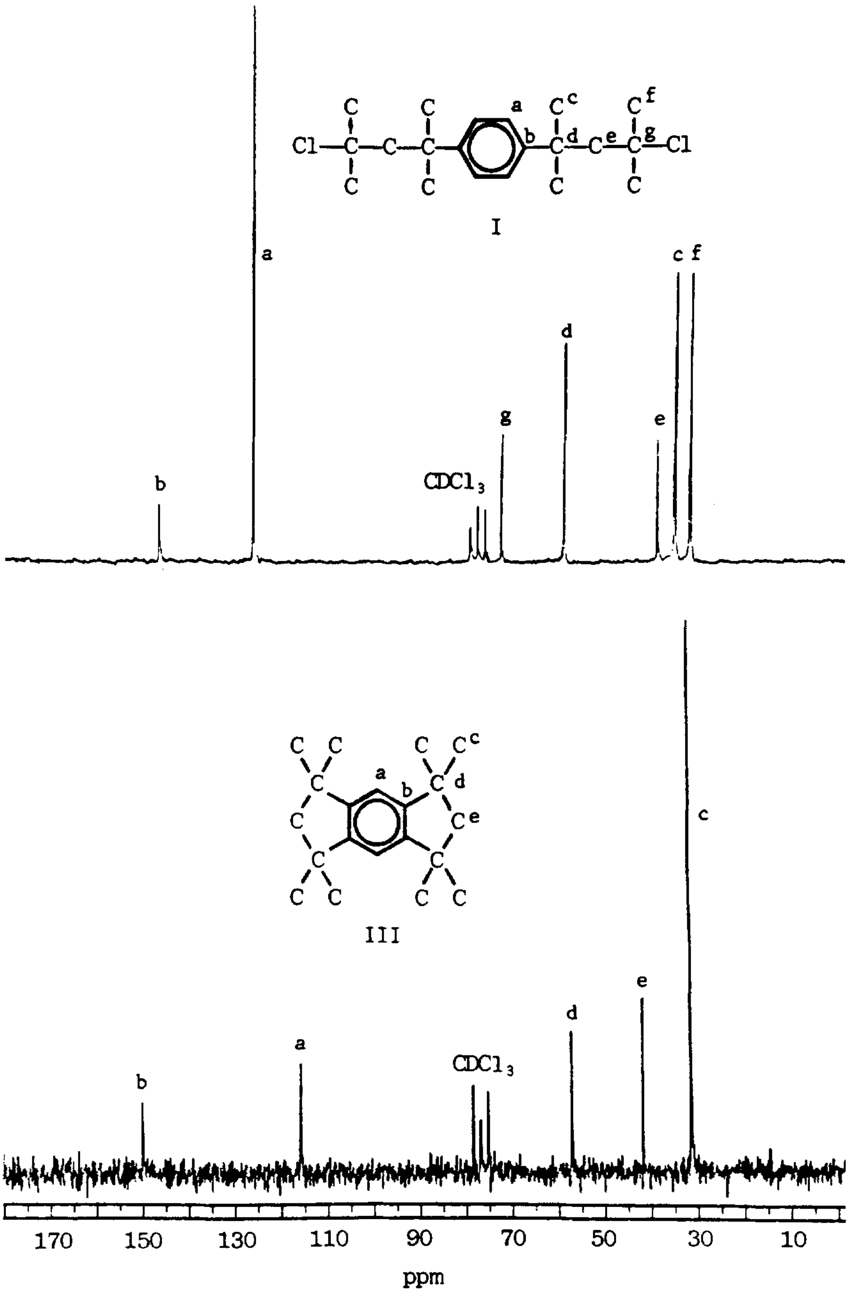


Figure 2. ^{13}C NMR Spectra of Model Compounds I and III.

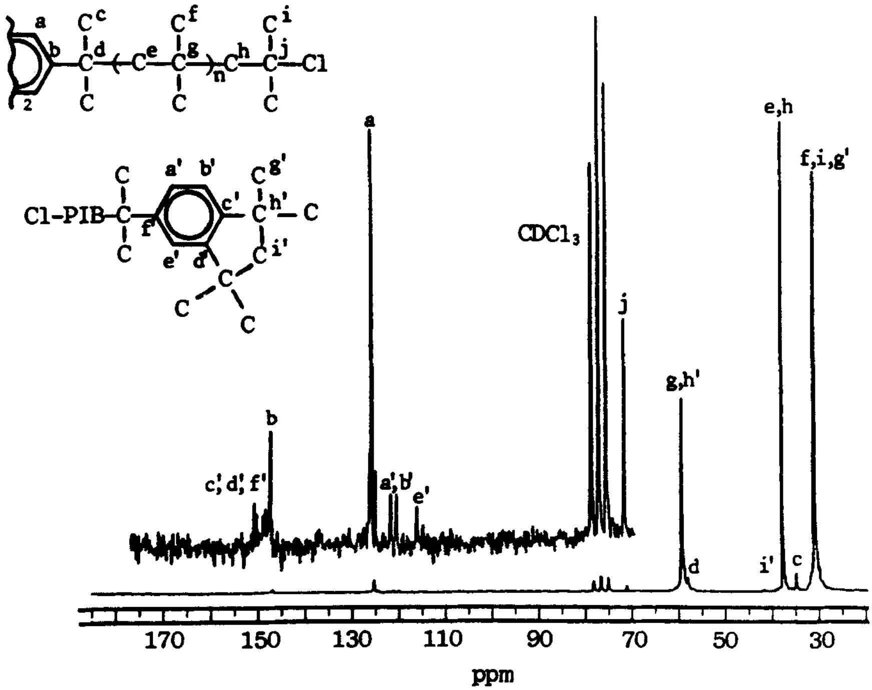


Figure 3. ^{13}C NMR Spectrum of Polyisobutylene Obtained at [pDCC]=2.0x10^{-2}M, [i-C_4H_8]=0.5M, [BCl_3]=6.0x10^{-2}M, -50°C, CH_3Cl Total Volume = 750 ml.

were measured by a Laboratory Devices Mel-Temp. instrument.

The Synthesis of the Inifer, p-dicumyl chloride, p-Bis(1-chloro-1-methylethyl)benzene. A 1 L three-neck flask was equipped with a mechanical stirrer, a Soxhlet extractor, and a reflux condenser, connected to a gas bubbler. The glassware was dried in a drying oven and assembled hot. The flask was cooled by purging with dry nitrogen through the top of the condenser. Supported by a small amount of glass wool, the extractor was filled with 48.5 g (0.25 mol) of dry dimethyl terephthalate, and 360 mL 3 M (1.1 mol) solution of methylmagnesium bromide in ethyl ether diluted with 500 mL anhydrous ethyl ether was added to the flask. The Grignard solution was gently stirred and refluxed, until the dimethyl terephalate was extracted into the flask. The light yellow dispersion that resulted was refluxed for an additional 3 h before it was allowed to cool to room temperature. The mixture was hydrolyzed by slowly pouring it over a stirred mixture of 600 mL 6 M H_2SO_4, 500 mL ethyl ether, and 500 g of crushed ice. The etheral layer was separated and the aqueous layer was extracted with additional batches of ether until the solid disappeared. The combined etheral solutions were washed with distilled water until neutral, dried over MgSO$_4$, filtered, and the solvent was removed. The crude product *p*-bis(1-hydroxyl-1-methylethyl)benzene was purified by recrystallizing twice from ethylacetate. The pure product was placed in a 500 mL three-neck flask fitted with a stirrer, a gas inlet, and a gas outlet tube connected to a HCl trap. After 100 mL dry methylene chloride and 20 g anhydrous calcium chloride were added to the flask, the system was cooled to 0°C. Then under stirring dry HCl gas was bled into the flask, until all suspended crystals dissolved. The solution was filtered, the solvent removed, and the crude product was recrystallized from *n*-hexane to give 18.5 g (32%)of I: mp. 71°C; ^{1}H NMR (CCl$_4$) δ 1.95 (methyl, s, 12H), 7.40 (aromatic, s, 4H).

p-Bis(3-chloro-1,1,3-trimethylbutyl)benzene (I). In a stainless steel enclosure under a dry nitrogen atmosphere 3.0 g (13 mmol) pure p-dicumyl chloride were dissolved in a culture tube in a mixture of dry CH$_2$Cl$_2$ and n-hexane (20 mL: 20 mL). The solvents were distilled under dry nitrogen over calcium hydride. The mixture was cooled to -40°C, 2.3 mL (13.7 mmol) isobutylene were added at -40°C with a prechilled pipet and 4.0 mL (49.8 mmol) BCl$_3$ were introduced at -40°C. After 10 min of constant shaking, 3 mL prechilled methanol were added at -40°C; the mixture was washed with 30 mL 0.5N HCl, 30 mL distilled water and dried over MgSO$_4$. Finally the solvent was removed to give 4.1 g (92%) of I: mp. 70°C; IR (CCl$_4$) 1910 (w), 1660 (w), 1230 (m), 1130 (s) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 1.25 (methyl, s, 12H), 1.45 (methyl, s, 12H), 2.30 (methylene, 2, 4H), 7.20 (aromatic, s, 4H); ^{13}C NMR (CDCl$_3$) δ 146.7 (C$_4$, aromatic), 126.3 (aromatic), 72.4(C$_4$,C-Cl), 58.8 (C$_4$,C-Ø), 38.7 (methylene), 34.8 (methyl), 31.6 (methyl).

p-Bis(1,1,3-trimethyl-3-butenyl)benzene (II). In a 100 mL three-neck flask fitted with an addition funnel, a reflux condenser, and a gas inlet tube were added 1.0 g (2.9 mmol) I and 20 mL dry tetrahydrofuran freshly distilled over lithium aluminum hydride under dry nitrogen. The solution was heated to reflux and 1.36 g (11.6 mmol) potassium *t*-butoxide in 10 mL dry tetrahydrofuran was added over 5 min with stirring. After an additional 20 min at reflux temperature, the flask was cooled to room temperature, 30 mL ethyl were added to the reaction mixture, washed with two portions of 50 mL distilled water, and the aqueous layer was twice extracted with 20 mL ether. The combined etheral solutions were dried over MgSO$_4$, filtered, and the solvent was removed to give 0.65 g (83%) of II: IR

(CCl_4) 3075 (s), 1900 (w), 1780 (m), 1630 (s), 890 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.3 (methyl, 2s, 18H), 2.3 (methylene, br s, 4H), 4.4 (vinylidene, cis to methyl, s of m, 2H), 4.7 (vinylidene, trans to methyl, s of m, 2H), 7.2 (aromatic, s, 4H).

1,1,3,3,5,5,7,7-Octamethyl-s-hydrindacene (III). In a stainless steel enclosure under a dry nitrogen atmosphere 3.0 g (13 mmol) pure p-dicumyl chloride was dissolved at -40°C in 40 mL methylene chloride in a culture tube. Then 2.3 mL (13.7 mmol) isobutylene and 4.0 mL (49.8 mmol) BCl_3 were added under shaking at -40°C. After 10 min of shaking, the reaction mixture was purified by washing with 30 mL 0.5N HCl, 30 mL distilled water, dried over $MgSO_4$, and the solvent was removed. The crude product was recrystallized from ethyl ether to give 1.58 g (45%) of III: mp. 210°C; IR (CCl_4) 1750 (w), 1470 (m), 1450 (m), 1370 (w), 1360 (m), 1310 (m), 1290 (m), 1240 (m) cm^{-1}; ^1H NMR (CCl_4) δ 1.32 (methyl, s, 24H), 1.87 (methylene, s, 4H), 6.62 (aromatic, s, 2H); ^{13}C NMR ($CDCl_3$) δ 150.5 (C_4, aromatic), 116.4 (aromatic), 57.9 (C_4, aliphatic), 42.7 (methylene), 32.3 (methyl).

Alternative Synthesis of III. The reaction mixture obtained in the synthesis of I prior to addition was warmed to and stored at room temperature under nitrogen atmosphere for three days. Subsequently the solution was washed with 30 mL 0.5N HCl, 30 mL distilled water, dried over $MgSO_4$, the solvent removed, and recrystallized from ether to give 3.05 g (87%) of III.

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