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New Telechelic Polymers and Sequential Copolymers by Polyfunctional *Ini*tiator-Trans*fer* Agents (Inifers)

29. Synthesis of α,ω-Di(Amino)Polyisobutylenes

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SUMMARY

A variety of primary and tertiary amino-telechelic polyisobutylenes have been synthesized quantitatively by various routes from alcohol-telechelic polyisobutylene. Thus the syntheses of α,ω-di(amino)-, α,ω-di-(N,N'-dimethylamino)-, and α,ω-di(N-phthalimido)polyisobutylenes have been achieved from α,ω-di(hydroxy)polyisobutylene with and without chain enlargement. Three different methods were used: an improved Gabriel synthesis, the reaction of ditosylester of α,ω-di(hydroxy)polyisobutylene with the potassium salt of unsubstituted and disubstituted ethanolamine, and the reduction of α,ω-di(cyanoethanol)polyisobutylene with $LiAlH_4$ at room temperature. Analysis and characterization were done by gel permeation chromatography, IR and ^{1}H-NMR spectroscopy.

INTRODUCTION

Amino-telechelic polyisobutylenes (PIB's) have been prepared from alcohol-telechelic PIB's. Three methods are most frequently used to replace hydroxyl end groups by amino groups: Gabriel synthesis leading to the replacement of hydroxyl groups by amino groups without chain extension (1), Gabriel synthesis with chain extension (2), and the reaction of ditosyl esters of α,ω-dihydroxy derivatives with the potassium salt of unsubstituted or substituted ethanolamine (3). The latter method proposed by Kern et al. (3) consists of a two step reaction (one less than the Gabriel synthesis) and also leads to chain enlargement. Recently Ziegast and Pfannemuller (4) investigated a great variety of procedures to convert hydroxyl end groups of polyoxyethylene by amino groups. The extent of conversion was determined by ^{13}C-NMR spectroscopy. According to these authors Kern's method is simpler and it yields quantitative conversion of -OH groups. The Gabriel synthesis is rather inconvenient mainly because of difficulties arising during the conversion of the alkyl phthalimide. This reaction is usually carried out in anhydrous dipolar aprotic solvents, generally DMF, which is a nonsolvent for PIB. Consequently only by the use of a phase transfer catalyst can this reaction step be accomplished quantitatively and the data in the literature suggest an excellent method which may give rise to 100% conversion (5). The first step in the Gabriel synthesis, i.e., tosylation or methanesulfonation of the primary alcohol may also yield less than 100% conversion. Recently improved procedures have been worked out and these reactions yield quantitative conversions in the case of α,ω-di(hydroxy)PIB (6,7). In view of these improvements in the methodology -OH groups can be quantitatively replaced by amino groups even by the Gabriel method.

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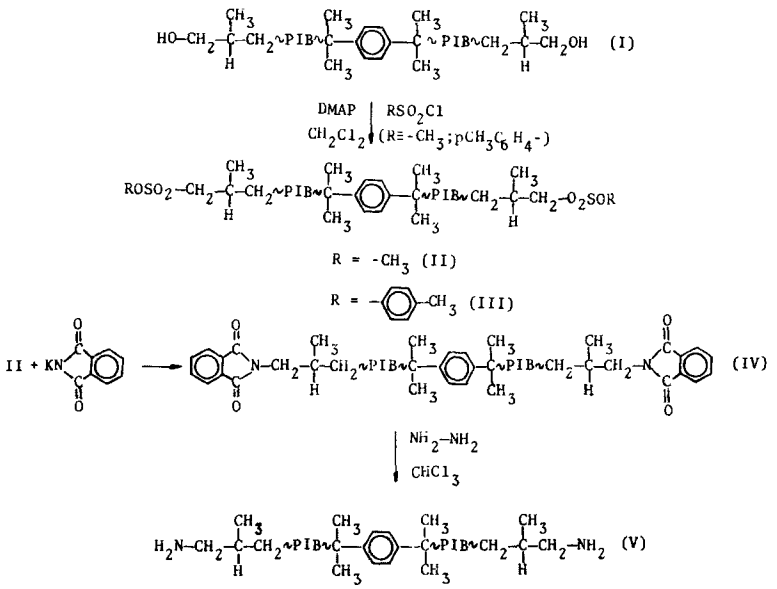
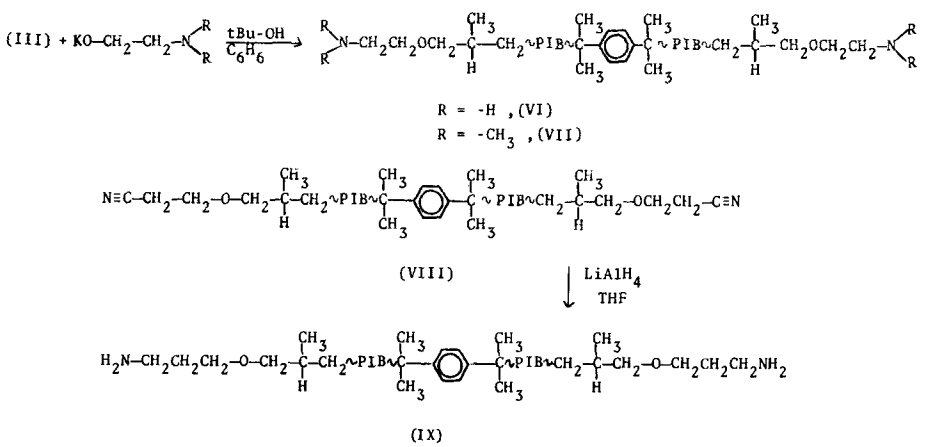
This paper concerns the synthesis of α,ω-di(amino)PIB and α,ω-di-(N,N'-dimethylamino)PIB by using Kern's method by an improved Gabriel synthesis without chain enlargement, and by the reduction of dicyanoethylated PIB. Schemes 1 and 2 show the transformations investigated.



Scheme 1: Synthesis of α,ω-di(methanesulfonyl)- (II), α,ω-di(tosyl)- (III) and α,ω-di(amino)polyisobutylenes (V).



Scheme 2: Synthesis of α,ω-di(amino)polyisobutylenes (VI and IX) and of α,ω-di(N,N'-dimethylamino)polyisobutylene (VII).

MATERIALS AND TECHNIQUES

The synthesis of α,ω-di(hydroxy)PIB with $\bar{F}_n$= 2 (8) and experimental and instrumental techniques have been described (6). Potassium phthalimide (Aldrich), hydrazine hydrate (100%, Aldrich), methanesulfonyl chloride (Eastman), p-toluenesulfonyl chloride (Eastman), 4-N,N'-dimethylaminopyridine DMAP (Aldrich), and tricaprylylmethylammonium chloride (Aliquat 336, Aldrich) were used as received. The solvents were carefully dried and distilled under nitrogen.

SYNTHESIS AND RESULTS

The synthetic procedures are presented in Schemes 1 and 2. The roman numerals in this section refer to Scheme 1 or 2. The tosylation and methanesulfonation of α,ω-di(hydroxy)PIB (compounds II and III) have been described previously (6,7).

Synthesis of α,ω-di(N-phthalimide)PIB IV. A toluene solution (50 ml) of 2 g II ($\bar{M}_n$= 4700, 0.43 mmole, 0.86 mmole methanesulfonic ester), 0.32 g potassium phthalimide (1.72 mmole) and 0.1 g Aliquat 336 was stirred at 100°C for 20 hours. The reaction mixture was cooled, filtered, washed with 10% aqueous NaOH till neutral, dried over anhydrous $MgSO_4$ and the solvent was evaporated. The product was dissolved in hexanes, filtered, and precipitated twice from acetone. IR:1762 cm^{-1} (νC=O asymmetric), 1700 cm^{-1} (νC=O symmetric), 1600 cm^{-1} (νC=C aromatic). NMR(CCl_4,TMS): δ = 7.75 ppm (8 aromatic protons from terminal phthalimide group), δ = 7.2 ppm (4 aromatic protons from central inifer group), δ = 3.45 ppm ($-C\underline{H}_2N$) (Figure 1). According to the ratio of the areas under the signals at δ = 7.75 and δ = 7.20 ppm ($A\delta_{7.75}/A\delta_{7.20}$ = 2/1), and to the shift of the resonance from δ = 3.2 ppm to 3.45 ppm associated with the $C\underline{H}_2O$ protons, the conversion of II to IV was considered quantitative.

Synthesis of α,ω-di(amino)PIB V. To a refluxing solution of IV in 10 ml chloroform and 10 ml ethanol was added while stirring 10 ml (large excess) hydrazine hydrate. After refluxing for 40 hours, the mixture was cooled to 0°C, acidified with concentrated hydrochloric acid, and refluxed again for 1 hour. The precipitated phthalyl hydrazide was filtered off and the solvent was evaporated. The product was dissolved in hexanes, washed with NaOH (10% solution), water, dried over anhydrous $MgSO_4$ and then precipitated twice from acetone. The IR spectrum is void of carbonyl absorption and the $-NH_2$ absorptions are very weak because of the high molecular weight of the product ($\bar{M}_n$= 4700). ^{1}H-NMR (CCl_4, TMS) δ = 7.17 ppm (4 aromatic protons from inifer) (Figure 1c). The complete absence of the usually strong νC=O absorptions at 1762 , and 1700 cm^{-1} in the IR spectrum suggests quantitative conversion of N-phthalimide to $-NH_2$ group.

Synthesis of α,ω-di(amino)PIB VI. To 0.6 g (5.3 mmole) potassium t-butoxide dissolved in 10 ml dry t-butanol were added 15 ml dry benzene and 0.20 g (3.3 mmole) ethanolamine. After the solution was heated to a mild boiling, 0.65 g of α,ω-di(tosylated) PIB (III, $\bar{M}_n$ = 6000, 0.11 mmole which correspond to 0.22 mmole tosyl groups) dissolved in 10 ml benzene was added over a period of 5 minutes. The reaction mixture was refluxed for 10 hours and then allowed to stand overnight at room temperature. The precipitated salt was filtered off and the mother liquor was washed twice with 100 ml portions of an aqueous potassium hydroxide solution, then washed with water till neutral and dried over anhydrous $MgSO_4$.

The solvent was evaporated on a rotary evaporator and the polymer was dried. IR(KBr): 1100 cm^{-1} (νC-O-C). ^{1}H-NMR ($CDCl_3$, TMS): δ = 3.06 ppm (CH_2N, t and OCH_2PIB, d), δ = 3.43 ppm ($N-CH_2-CH_2O$, t) (Figure 2). The ratio of the areas of the resonances at δ = 7.17 ppm (aromatic) and δ = 3.06 plus δ = 3.43 ppm, i.e., $A\delta_{7.17}/(A\delta_{3.06} + A\delta_{3.43})$, is 1/3 which indicates quantitative conversion.

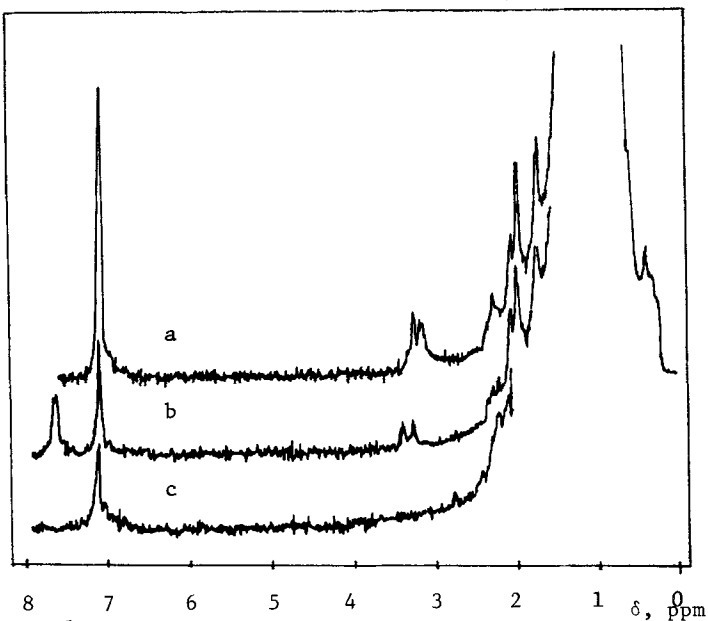


Figure 1. ^{1}H-NMR spectra of: a) α,ω-di(hydroxy)polyisobutylene (I), b) α,ω-di(N-phthalimido)polyisobutylene (IV), and c) α,ω-di(amino)polyisobutylene (V)

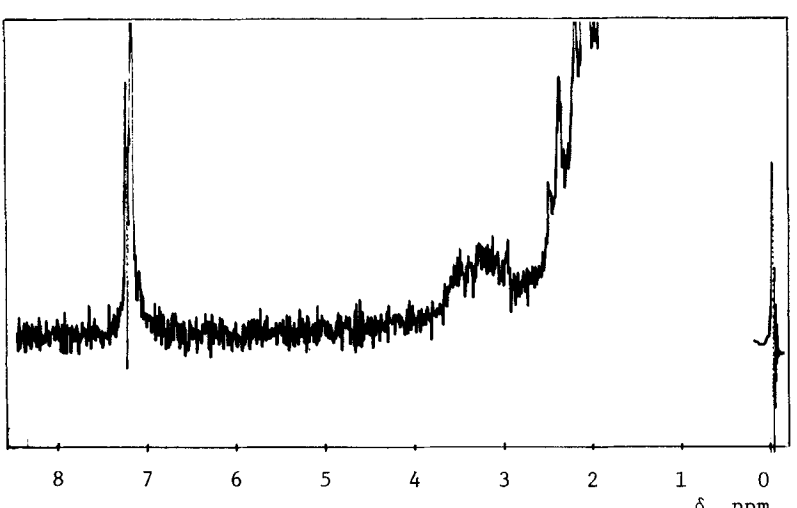


Figure 2. ^{1}H-NMR spectrum of α,ω-di(amino)polyisobutylene (VI)

Synthesis of α,ω-di(N-dimethylamino)PIB VII. This compound was synthesized in the same manner as compound VI except that monoethanolamine was replaced by N-dimethylethanolamine. The IR and NMR spectra of VII (Figure 3) are identical with those of VI. The N-methyl resonances in the NMR spectrum are masked by the CH_3 and CH_2 resonances of PIB. The ratio $A\delta_{7.17}/(A\delta_{3.06} + A\delta_{3.43}) = 1/3$ (see above) indicates quantitative end group conversion.

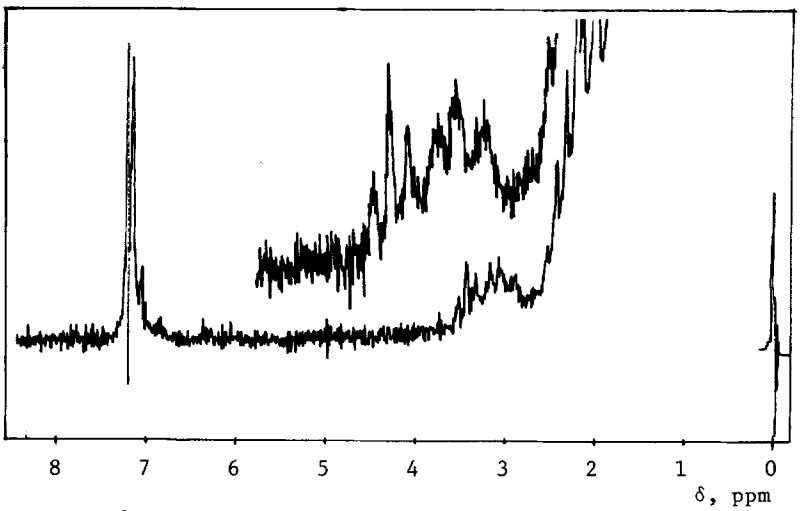


Figure 3. ^{1}H-NMR spectrum of α,ω-di(N-dimethylamino)polyisobutylene (VII)

Synthesis of α,ω-di(amino)PIB IX. Product IX was synthesized by reduction of α,ω-di(cyanoethanol)PIB (VIII) with excess $LiAlH_4$ at room temperature in THF (reaction time 20 hours). Compound VIII was obtained by cyanoethylation of α,ω-di(hydroxy)polyisobutylene (7). Compound IX was separated from $LiAlO_2$ and excess $LiAlH_4$ by filtration. It showed the same spectral characteristics as compound VI obtained by the Kern method. The experimental difficulties are due to the separation of α,ω-di(amino)PIB from $LiAlO_2$ and unreacted $LiAlH_4$. The IR spectrum of IX is completely void of the absorption due to ν C≡N (2250 cm^{-1}) which indicates quantitative reduction of VIII.

CONCLUSIONS

Starting with α,ω-di(hydroxy)polyisobutylene several procedures have been developed for the synthesis of both primary and tertiary aminotelechelic polyisobutylenes. These α,ω-di(amino)polyisobutylenes represent valuable intermediates for the synthesis of new polymeric materials.

ACKNOWLEDGEMENT

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