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Oxyethylation and carbonation of telechelic polyisobutylene anions

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SUMMARY

The synthesis of $(CH_3)_3C\sim PIB\sim CH_2C(=CH_2)CH_2CH_2CH_2OH$ and $(CH_3)_3C\sim PIB\sim CH_2(=CH_2)CH_2COOH$ have been achieved by oxyethylation and carbonation of telechelic polyisobutylene anions: $(CH_3)_3C\sim PIB\sim CH_2C(=CH_2)CH_2^{\ominus}$. The latter macroanions were prepared from $(CH_3)_3C\sim PIB\sim CH_2C(CH_3)_2Cl$ by one-pot dehydrochlorination-metalation with n-BuLi/t-BuOK in hexanes. The structure of the products was established by detailed ^1H and ^{13}C NMR analyses which also involved the characterization of 4-neopentyl-4-penten-1-ol and 3-neopentyl-3-butenoic acid model compounds.

I. INTRODUCTION

The chain-end functionalization of living carbanionic polymers has been thoroughly studied and often reviewed (1-5). The quantitative allylic lithiation of isopropylidene-capped PIBs ($PIB\sim CH_2C(=CH_2)CH_3$) and dehydrochlorination-lithiation of t-chlorine-capped PIBs ($PIB-CH_2C(CH_3)_2Cl$) has been accomplished using BuLi/TMEDA (N,N,N',N'-tetramethylethylenediamine) (6-7). This metalating reagent in combination with ethylene oxide (EO) yields essentially quantitative oxyethylation of lithiated PIB (8). The number-average hydroxyl chain-end functionality of oxyethylated PIB was however ∿5% higher than theoretical due to dilithiation at the chain ends (6,7). The oxyethylated chain-ends carried $-CH_2CH_2OH$ and $-CH_2CH_2OCH_2CH_2OH$ groups (8).

Improved functionalizations have now been obtained by the use of the more reactive and selective n-BuLi/t-BuOK combination in hexanes solvent. Conditions leading to quantitative oxyethyethylation and close to quantitative carbonation of PIB-anions have been worked out first on model compounds and then adapted for polymers:

Model Studies:

$$(CH_3)_3CCH_2C(=CH_2)CH_3 \xrightarrow[-H^{\oplus}]{\text{n-BuLi/t-BuOK}} (CH_3)_3CCH_2C(=CH_2)CH_2^{\ominus}$$

$$\xrightarrow{EO/H^{\oplus}} (CH_3)_3CCH_2C(=CH_2)CH_2CH_2CH_2OH$$

$$\xrightarrow{CO_2/H^{\oplus}} (CH_3)_3CCH_2C(=CH_2)CH_2COOH$$

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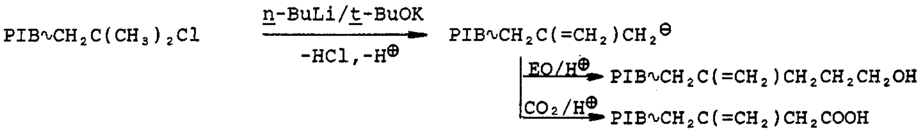
Polymer Studies:



$$PIB\sim CH_2C(CH_3)_2Cl \xrightarrow[-HCl,-H^{\oplus}]{n\text{-BuLi}/t\text{-BuOK}} PIB\sim CH_2C(=CH_2)CH_2^{\ominus}$$

$$\xrightarrow{EO/H^{\oplus}} PIB\sim CH_2C(=CH_2)CH_2CH_2CH_2OH$$

$$\xrightarrow{CO_2/H^{\oplus}} PIB\sim CH_2C(=CH_2)CH_2COOH$$

Oxyethylation and carbonation of PIB$^{\ominus}$ anions were carried out in the absence of side reactions. Under well-defined conditions (low temperature, short reaction time) multiple EO addition can be avoided and functionalization with one single EO unit can be effected. Protonation yields polymers fitted with one terminal $-CH_2CH_2OH$ function.

In regard to carbonation, the absence of side reactions may be due to active terminal anions arising with n-BuLi/t-BuOK to form mixed aggregates of $(CH_3)_3C\sim PIB\sim CH_2C(=CH_2)CH_2^{\ominus}K^{\oplus}$ plus t-BuOLi (9-11) which quantitatively yield acids with CO_2. The t-BuOLi arises during transmetalation between n-BuLi and t-BuOK (11). In line with our results Pannell has reported that poly(styryl)K reacts with carbon dioxide without side reactions (12).

II. EXPERIMENTAL

a) Materials

Olefin-free hexanes were prepared by a standard procedure (6). 2,4,4-Trimethyl-1-pentene (TM1P) (Aldrich) was distilled over CaH_2 before use. n-Butyllithium (n-BuLi, 1.6 M solution in hexanes, Aldrich), potassium-t-butoxide (t-BuOK, Aldrich), ethylene oxide (EO, Fluka) and Dry-Ice were used as received. 2-Chloro-2,4,4-trimethylpentane (TMPCl) was prepared from TM1P by hydrochlorination (13). The $(CH_3)_3C\sim\sim PIB\sim\sim CH_2C(CH_3)_2Cl$ (PIB-Cl^{t}) was prepared by the polymerization of isobutylene using the TMPCl/BCl_3/N,N-dimethylacetamide/CH_3Cl/-45°C system (14).

b) Characterization methods

^1H NMR and ^{13}C NMR spectra were obtained with a Varian Gemini-200 spectrometer using $CDCl_3$ solutions ($\sim$15 and $\sim$30% w/v) at ambient temperature. The ^1H NMR spectra were recorded at 200 MHz (the main parameters were: pulse width = 14.5 μs; pulse delay = 20s; acquisition time = 5.0s; number of transients = 16; number of data points = 30,016). The ^{13}C NMR spectra were recorded at 50.3 MHz under conditions detailed in our previous publication (16). Assignments are given in ppm's; in case of multiplets the multiplet center is indicated.

Molecular weights ($\overline{M}_n$) and dispersities ($\overline{M}_w/\overline{M}_n$) were determined by a Waters high pressure GPC instrument equipped with dual RI and UV detectors and five μ-Styragel columns. The calibration curve was constructed of narrow MWD PIB standards (15).

c) Synthesis Procedures

1) Metalation of 2,4,4-trimethyl-1-pentene

TM1P (11.22 g, 100 mmol) in 50 g hexanes, t-BuOK (14.1 g, 125 mmol) and n-BuLi (78.2 mL 1.6 M in hexanes, 125 mmol) were agitated in a septum-capped 250 mL round-bottom flask under nitrogen for 3 hrs at room temperature. This reaction mixture was used for oxyethylation and carbonation.

2) "One-pot" dehydrochlorination-metalation of PIB-Cl$^{\underline{t}}$

PIB-Cl$^{\underline{t}}$ (11.30 g; $\overline{M}_n$ = 1130, $\overline{M}_w/\overline{M}_n$ = 1.11; 10 mmol) in 25 g hexanes, t-BuOK (6.73 g, 60 mmol), and n-BuLi (37.5 mL 1.6 M in hexanes, 60 mmol) were agitated in a septum-capped 250 mL round-bottom flask under nitrogen for 5 hrs at room temperature. The above reaction mixture was used for oxyethylation and carbonation.

3) Oxyethylation of TM1P$^{\ominus}$ and PIB$^{\ominus}$ anions

The dark-brown metalating system was cooled in an acetone-Dry Ice bath and an excess of EO (EO/n-BuLi $\sim$15) was added. During the agitation the reaction mixture was allowed to warm up. Gradually the charge became light yellow ($\sim$20 min). After stirring an additional 20 minutes, the charge was poured into an excess of 5% aqueous hydrochloric acid and was stirred for several hours. The organic phase was washed with distilled water until neutral.

For oxyethylation of the model compound, the hexanes were allowed to evaporate at room temperature; conversion $\sim$100% (by ^{1}H NMR based on the disappearance of the characteristic resonance $(CH_3)_3CCH_2C(=CH_2)C\underline{H}_3$ at δ = 1.78 ppm). The 4-neopentyl-4-penten-1-ol was obtained by distilling over molecular sieves under reduced pressure; yield $\sim$93%.

The functionalized PIB was dissolved in hexanes, precipitated in methanol, redissolved in hexanes, dried over molecular sieves, the hexanes were evaporated (rotovap), and the polymer was dried under vacuum. The purified polymers were characterized by NMR spectroscopy and GPC. PIB conversion $\sim$100% (by ^{13}C NMR based on the disappearance of the characteristic resonances of $PIB\sim\underline{C}H_2\underline{C}(=\underline{C}H_2)\underline{C}H_3$ at δ = 54.03, 144.27, 114.97 and 26.01 ppm (16)).

4) Carbonation of TM1P$^{\ominus}$ and PIB$^{\ominus}$anions

The dark-brown charge containing TM1P$^{\ominus}$ or PIB$^{\ominus}$ was transferred under constant agitation under a blanket of nitrogen into a 2 L flask containing a large amount of freshly crushed Dry-Ice (17). This flask was then equipped with a drying tube and stored for overnight. The protonation of the carboxylated model compound and PIB were accomplished by mixing the charges with 5% aqueous HCl for several hours (A separate experiment showed that the use of methanolic HCl caused esterification of the model carboxylic acid). The organic phase was washed with distilled water until neutral.

From the solution of 3-neopentyl-3-butenoic acid, the hexanes were allowed to evaporate at room temperature. Conversion $\sim$100% (by H NMR, see above). The carboxylated model compound was obtained by distilling over molecular sieves under reduced pressure; yield ∿95%.

The carboxylated PIB was further purified by treating it in a large amount of boiling water (to remove by steam low molecular weight carboxylic acid impurities) followed by reprecipitation from hexanes into acetone, redissolution in hexane, drying over molecular sieves, and evaporating the hexanes. The polymer was dried under vacuum and analyzed by NMR spectroscopy and GPC. PIB conversion ∿97% (by ^{1}H NMR).

III. RESULTS AND DISCUSSION

The metalating charges with the precursors were not analyzed, only the products. According to ^{1}H and ^{13}C NMR analyses (see below) the products cannot be due to dianions. Thus only the monoanion is formed in the presence of the excess metalating reagent.

Figure 1a and 1b show the ^{1}H and ^{13}C NMR spectra of 4-neopentyl-4-penten-1-ol with assignments. The chemical shift of the -OH varies between 1 and 5 ppm depending on the concentration and can be removed with D_2O (-OD gives no signal) (18-19).

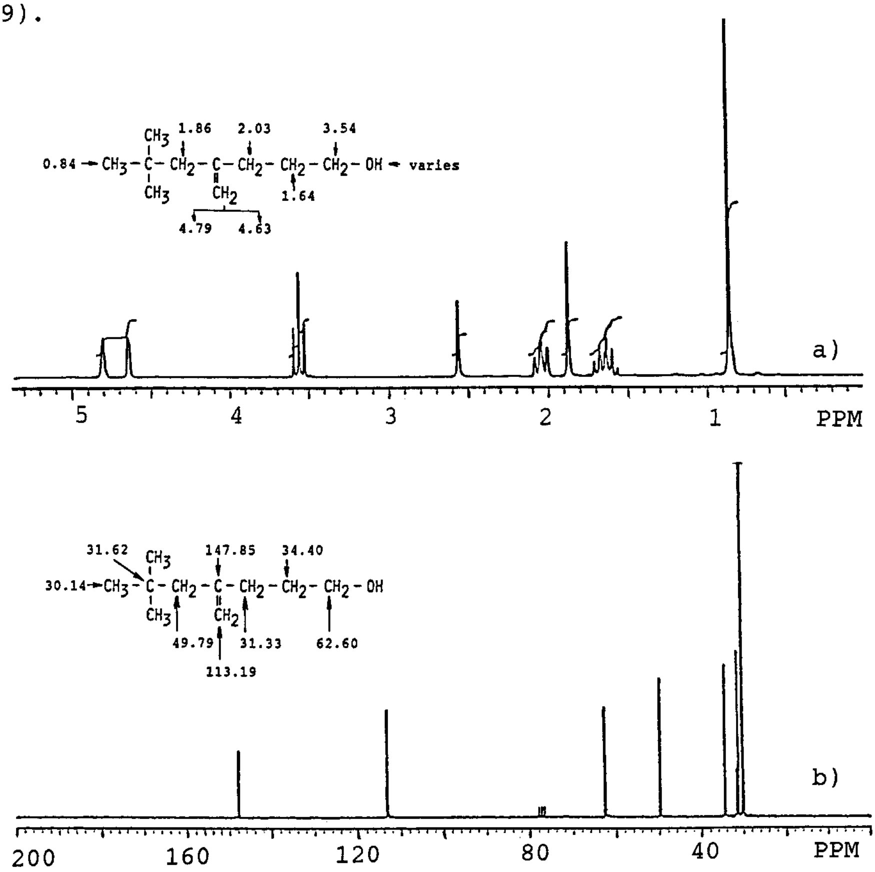


Figure 1. ^{1}H(a) and ^{13}C(b) NMR spectra of $(CH_3)_3CCH_2C(=CH_2)CH_2CH_2CH_2OH$

Figures 2 and 3 show the ^1H and ^{13}C NMR spectra of oxyethylated PIB ($\overline{M}_n$ = 1220; $\overline{M}_w/\overline{M}_n$ = 1.13) with assignments. The -OH proton peak is hidden due to its low concentration (19). Indirect determination of the number average -OH end functionality based on the ratio of integrated relative intensities of chain end protons: PIB∿C$\underline{H}_2$C(=C$\underline{H}_2$)C$\underline{H}_2$CH$_2$C$\underline{H}_2$OH gives $\overline{F}_n$ = 1.00± 0.02. The ^{13}C NMR chemical shifts associated with the $(CH_3)_3C$∿ chain end are available elsewhere (16).

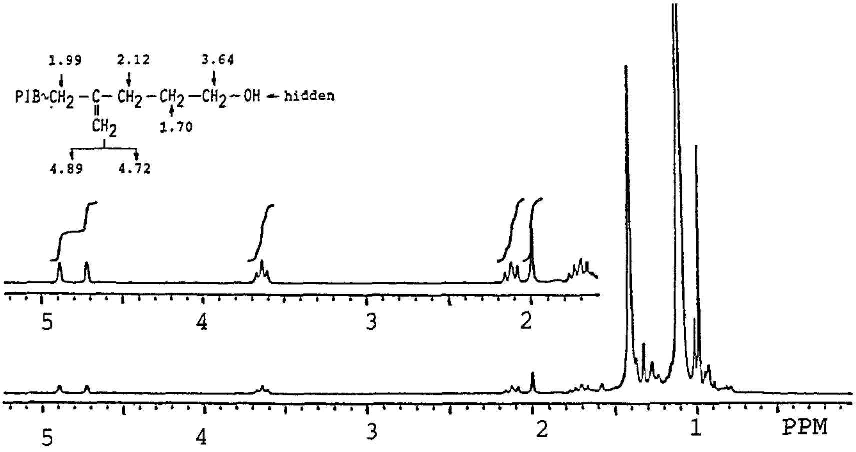


Figure 2. ^1H NMR spectrum of a $(CH_3)_3C$∿PIB∿CH$_2$C(=CH$_2$)-CH$_2$CH$_2$CH$_2$OH ($\overline{M}_n$ = 1220; M_w/M_n = 1.13)

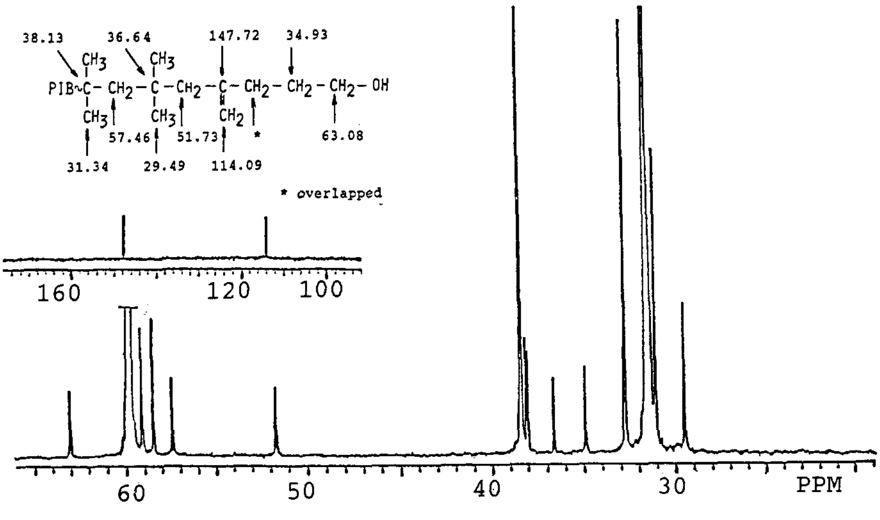


Figure 3. ^{13}C NMR spectrum of a $(CH_3)_3C$∿PIB∿CH$_2$C(=CH$_2$)-CH$_2$CH$_2$CH$_2$OH ($\overline{M}_n$ = 1220; M_w/M_n = 1.13)

Figures 4a and 4b show the ^{1}H and ^{13}C NMR spectra of 3-neopentyl-3-butenoic acid with assignments. The resonance characteristic of the -CoOH proton appears between 6 and 12 ppm, depending on the concentration. This resonance may be very broad and can be removed by D_2O (19).

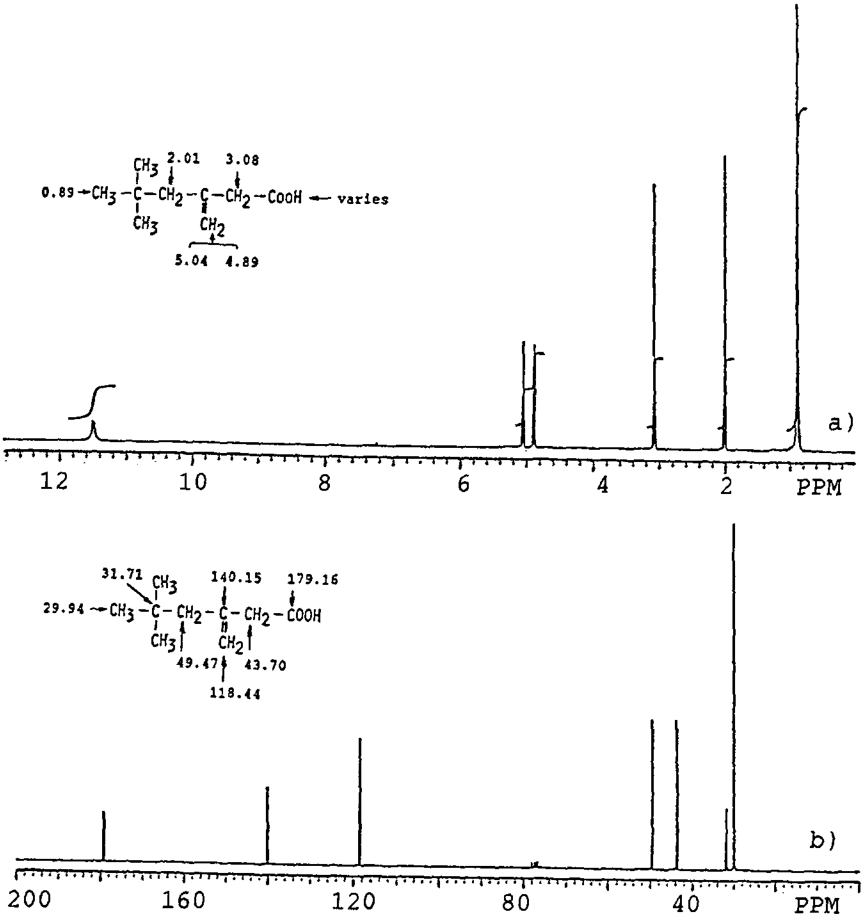


Figure 4. ^{1}H(a) and ^{13}C(b) NMR spectra of
$(CH_3)_3CCH_2C(=CH_2)CH_2COOH$

Figures 5 and 6 show the ^{1}H and ^{13}C NMR spectra of carboxylated PIB ($\overline{M}_n$ = 1260; $\overline{M}_w/\overline{M}_n$ = 1.15) with assignments. By amplifying the ^{1}H NMR spectra, resonances at 1.79, 2.00, 4.65 and 4.86 ppm became visible. According to this evidence we estimate that ∿3% of PIB$^{\ominus}$ anions was reconverted to PIB∿$CH_2C(=CH_2)CH_3$ which is most likely due to protogenic impurities in the CO_2 used.

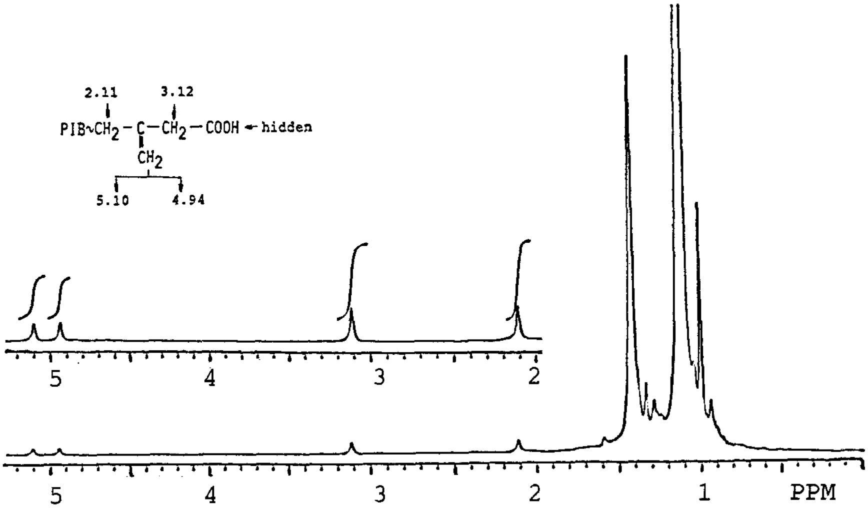


Figure 5. $^1\underline{H}$ NMR spectrum of a $(CH_3)_3C\sim PIB\sim CH_2C(=CH_2)CH_2COOH$ ($\bar{M}_n$ = 1260; $\bar{M}_w/\bar{M}_n$ = 1.15)

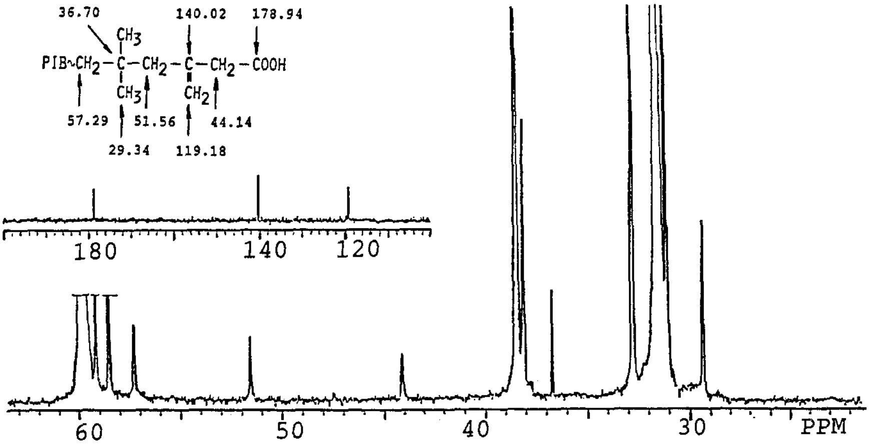


Figure 6. ^{13}C NMR spectrum of a $(CH_3)_3C\sim PIB\sim CH_2C(=CH_2)CH_2COOH$ ($\bar{M}_n$ = 1260; $\bar{M}_w/\bar{M}_n$ = 1.15)

The number average-COOH end functionality can be obtained indirectly by integrating the resonances associated with the chain end protons $\text{PIB}\sim C\underline{H}_2C(=C\underline{H}_2)C\underline{H}_2COOH$ $\bar{F}_n = 1.00 \pm 0.02$.

According to GPC analysis the $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ before and after carboxylation do not change within what is considered to be experimental error or due to purification.

ACKNOWLEDGEMENT

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