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Macromers by carbocationic polymerization

XI. Vinyl ether terminated polyisobutylenes*

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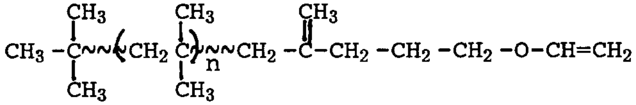
Summary

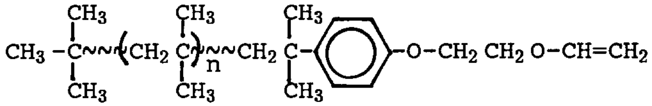
This communication describes the synthesis of two novel $CH_2=CH-O$-headed polyisobutylene(PIB)-based macromers:



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}\sim\sim\!\left(CH_2\underset{CH_3}{\overset{CH_3}{C}}\right)_n\!\sim\sim CH_2-\overset{CH_3}{\overset{\|}{C}}-CH_2-CH_2-CH_2-O-CH=CH_2$$

I

and



II

The syntheses were worked out by the help of model experiments and subsequently implemented on polymers. The structures were established by detailed ^1H and ^{13}C NMR spectroscopies.

I. Introduction

Research continues to be active world-wide on terminally functional polymers, specifically on macromers. This communication concerns the synthesis of the novel macromers I and II by a combination of largely carbocationic techniques. The following equations summarize the key transformations employed:

Model Reaction Sequence for the Synthesis of I:

$$(CH_3)_3CCH_2C(=CH_2)_2CH_3 \xrightarrow[-H^{\oplus}]{\underline{n}\text{-BuLi}/\underline{t}\text{-BuOK}} (CH_3)_3CCH_2C(=CH_2)CH_2^{\ominus}K^{\oplus}$$

$$\big\downarrow\ -KCl\quad +ClCH_2CH_2OCH=CH_2$$

$$(CH_3)_3CCH_2C(=CH_2)CH_2CH_2CH_2OCH=CH_2$$

Polymer Functionalization:

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

$$\xrightarrow[-KCl]{+ClCH_2CH_2OCH=CH_2} I$$

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*See J. P. Kennedy, S. Midha, A. Gadkari: J. Macromol. Sci. Chem., in press, for paper X in this series

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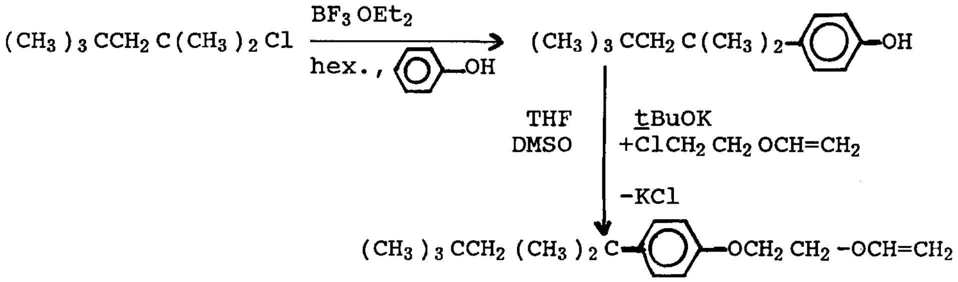
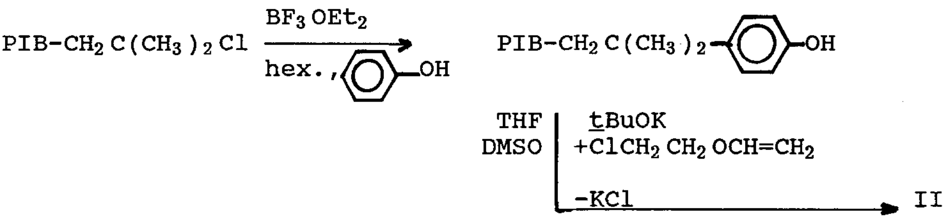
The n-BuLi/t-BuOK combination in hexanes solvent was shown to be an excellent quantitative metalating system (2-4).

Model Reaction Sequence for the Synthesis of II:



Polymer functionalization:



II. Experimental

a) Materials

Olefin free hexanes were prepared by a standard procedure (5). 2,4,4-Trimethyl-1-pentene (TM1P) (Aldrich) was distilled over CaH_2 before use. n-Butyllithium (1.6 M solution in hexanes) (Aldrich) and potassium-t-butoxide (Aldrich) were used as received. 2-Chloroethyl vinyl ether (Aldrich) was distilled over molecular sieves before use. 2-Chloro-2,4,4-trimethylpentane (TMPCl) was prepared from TM1P by hydrochlorination (6). The $(CH_3)_3C{\sim}PIB{\sim}CH_2C(CH_3)_2Cl$ (PIB-Cl^t) was prepared by the polymerization of isobutylene using the TMPCl/BCl_3/N,N-dimethyl-acetamide/CH_3Cl/−45°C system (7). All other solvents and chemicals were received from Aldrich and purified if needed as described in (11).

b) Characterization methods

^1H NMR and ^{13}C NMR spectra were obtained with a Varian Gemini-200 spectrometer using $CDCl_3$ solutions (~15 and ~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 = 20 s; acquisition time = 5.0 s; 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 (8). Assignments are given in ppm's.

Molecular weights ($\bar{M}_n$) and dispersities ($\bar{M}_w/\bar{M}_n$) 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(9).

c) Synthesis Procedures

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

TM1P (11.22 g, 100 mmol) in 50 g hexanes, potassium-*t*-butoxide (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 functionalization with 2-chloroethyl vinyl ether.

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

PIB-Cl$^{\underline{t}}$ (11.30 g; $\bar{M}_n$ = 1130, $\bar{M}_w/\bar{M}_n$ = 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 reacted for 5 hrs under the conditions described above.

3. Reaction of TM1P$^{\ominus}$ and PIB$^{\ominus}$ anions with 2-chloroethyl vinyl ether

The dark-brown metalating system prepared as described above was cooled to -78°C and an excess of 2-chloroethyl vinyl ether (2-chloroethyl vinyl ether/*n*-BuLi≈5) was added. The reaction mixture was allowed to warm to room temperature while stirring. Gradually the charge became light yellow (~30 min). After stirring for an additional 30 minutes, the charge was poured into an excess of distilled water and was stirred for several more hours. The organic phase was washed with distilled water until neutral. For the functionalization of the model compound, the hexanes were allowed to evaporate at room temperature. Conversion ~100% (by ^1H NMR based on the disappearance of characteristic resonance $(CH_3)_3CCH_2C(=CH_2)C\underline{H}_3$ at δ = 1.78 ppm), yield ~95%. The functionalized PIB was dissolved in hexanes, precipitated in methanol, redissolved, dried (molecular sieves), the hexanes evaporated (rotavap), and the polymer dried under vacuum. Conversion ~100% (by ^{13}C NMR based on the disappearance of characteristic resonances of PIB~$\underline{C}H_2\underline{C}(=\underline{C}H_2)\underline{C}H_3$ at δ = 54.03, 144.27, 114.97 and 26.01 ppm (8)). Figures 1a, 1b, 2 and 3 show the ^1H and ^{13}C NMR spectra of the products.

4. Phenolation of TMPCl and PIB-Cl$^{\underline{t}}$

In a 500 mL flask, equipped with a magnetic stirrer condenser, thermometer and an addition funnel were placed 18.8 g phenol (0.2 mol) and 2 mL BF_3OEt_2 (14 mmol) in 300 ml hexanes; then 3 g TMPCl (20 mmol), dissolved in 50 mL hexanes were added slowly (4 hrs) to the charge at 40-45°C. After 24 hrs 100 mL water were added, and the charge washed with water several times to remove the unreacted phenol. After drying over $CaCl_2$ the hexanes were evaporated and the product was recrystallized from hot methanol.

The phenolation of PIB-Cl$^{\underline{t}}$ was carried out in the same manner. The phenolations in both cases were quantitative (see Fig. 4a and 5a).

5. Reaction of p(2,2,4-trimethyl pentyl) phenol and phenol-ended PIB with 2-chloroethyl vinyl ether

The functionalization of phenol-ended PIB with 2-chloroethyl vinyl ether was carried out by an improved method

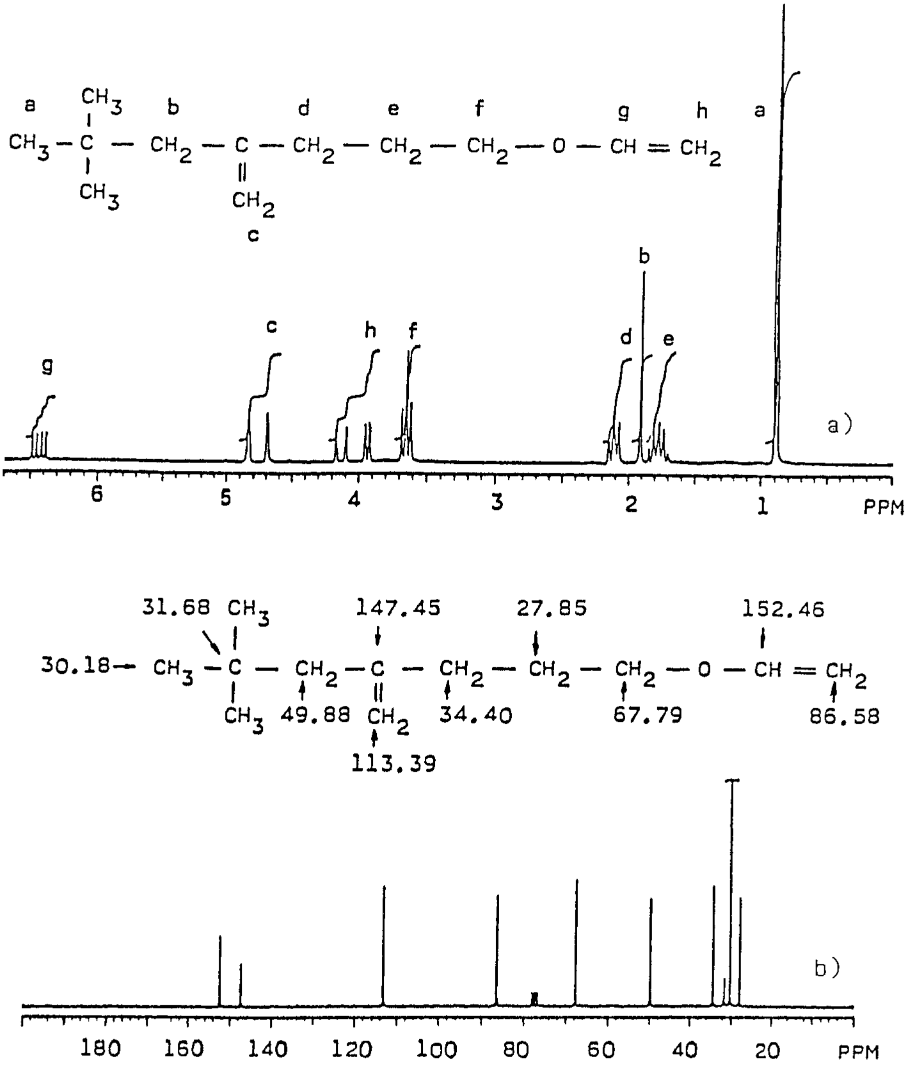


Figure 1. ^{1}H (a) and ^{13}C (b) NMR spectra of $(CH_3)_3CCH_2C(=CH_2)CH_2CH_2CH_2OCH=CH_2$ with assignments

described in ref 10. Thus, 2.06 g (~10 mmol) p(2,2,4-trimethyl pentyl) phenol and 3.4 g (33 mmol) tBuOK were dissolved in a mixture of 120 mL THF and 70 mL DMSO and heated to 70-75°C for 1 h. Then 3.5 mL (30 mmol) 2-chloroethyl vinyl ether in 20 ml DMSO were added slowly (~ 1 h) and the mixture heated for 5 more hrs at 70-75°C. Then the charge was poured into 200 mL water. The yellow organic layer was separated from the aqueous phase diluted with 100 mL hexanes, washed several times with water, dried over $CaCl_2$ and the hexanes were removed

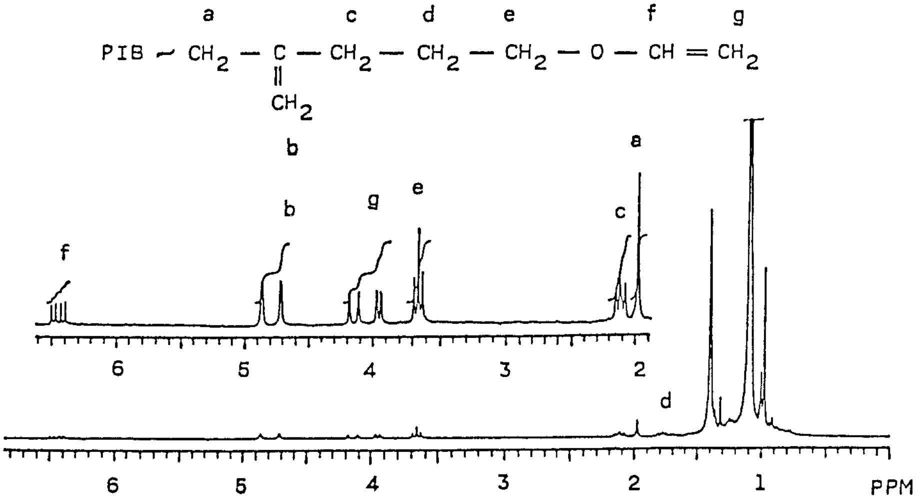


Figure 2. ^{1}H NMR spectrum of a $(CH_3)_3C\sim PIB\sim CH_2C(=CH_2)-CH_2CH_2CH_2OCH=CH_2$ ($\overline{M}_n = 1240$; $\overline{M}_w/\overline{M}_n = 1.12$) with assignments

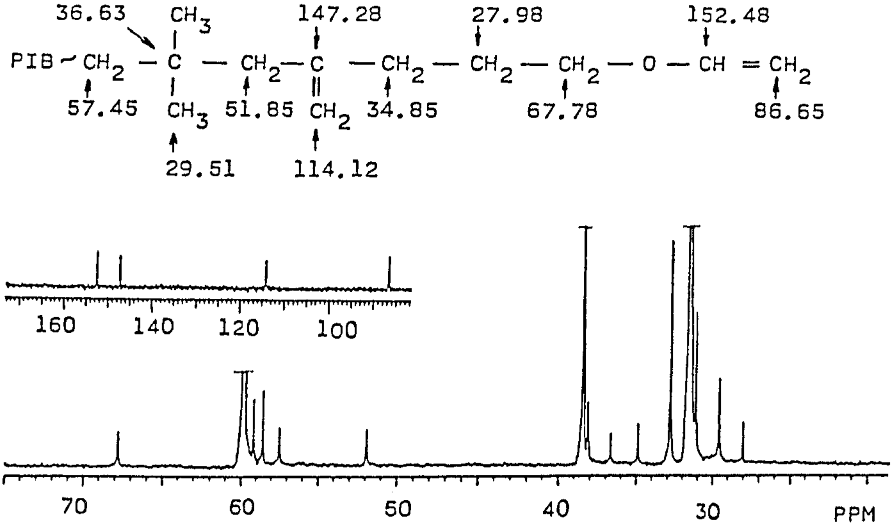


Figure 3. ^{13}C NMR spectrum of a $(CH_3)_3C\sim PIB\sim CH_2C(=CH_2)-CH_2CH_2CH_2OCH=CH_2$ ($\overline{M}_n = 1240$; $\overline{M}_w/\overline{M}_n = 1.12$) with assignments

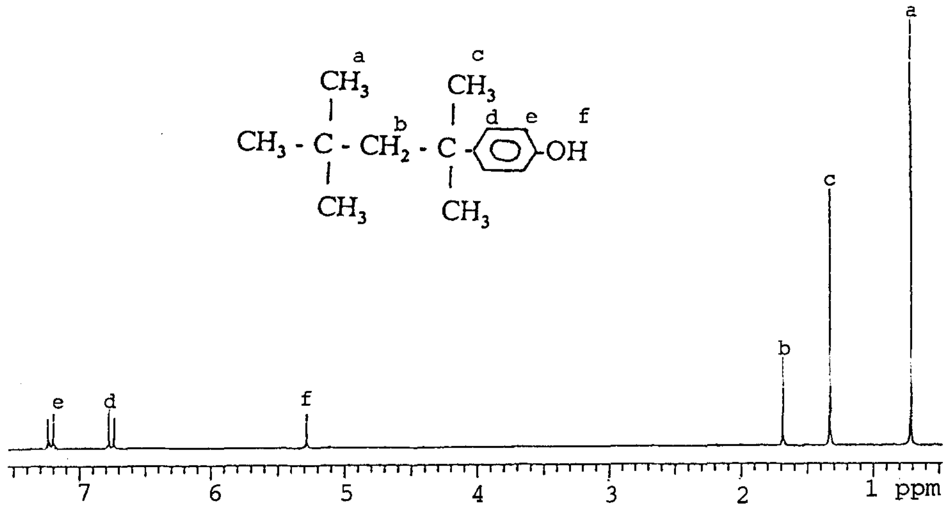


Figure 4a. ^{1}H NMR spectrum of p(2,2,4-trimethyl pentyl) phenol with assignments

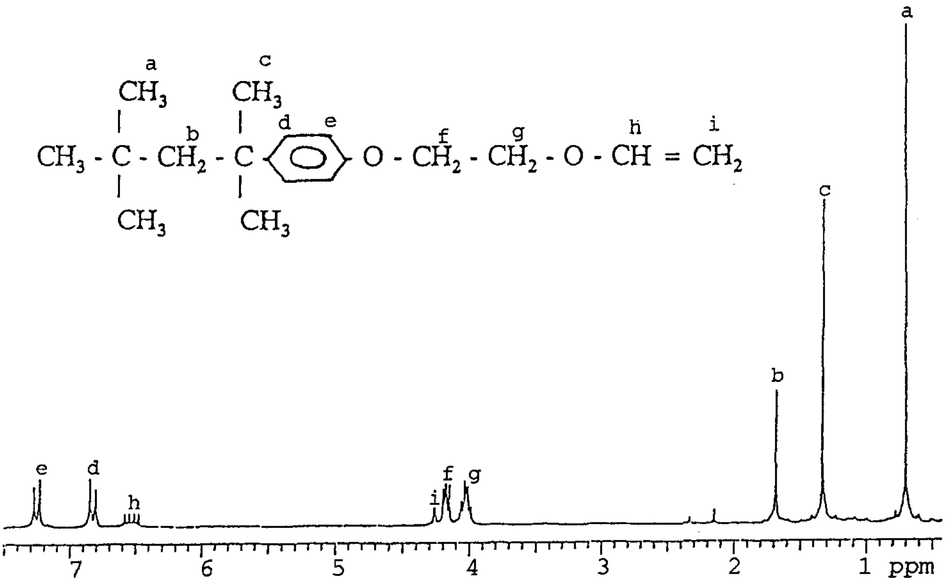
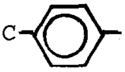


Figure 4b. ^{1}H NMR spectrum of $(CH_3)_3CCH_2(CH_3)_2C$- 
$OCH_2CH_2OCH=CH_2$ with assignments

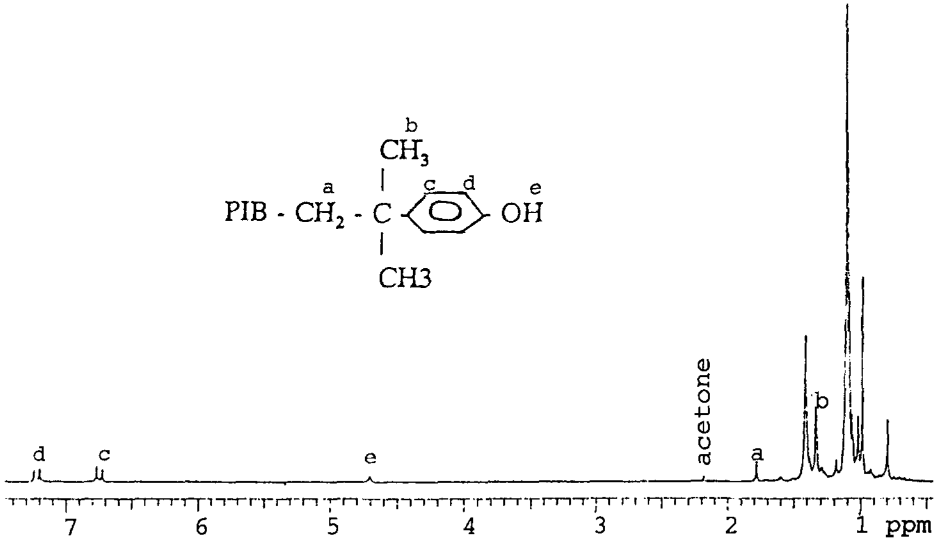


Figure 5a. ^{1}H NMR spectrum of a phenolated PIB with assignments ($\overline{M}_n$ = 1040; $\overline{M}_w/\overline{M}_n$ = 1.13)

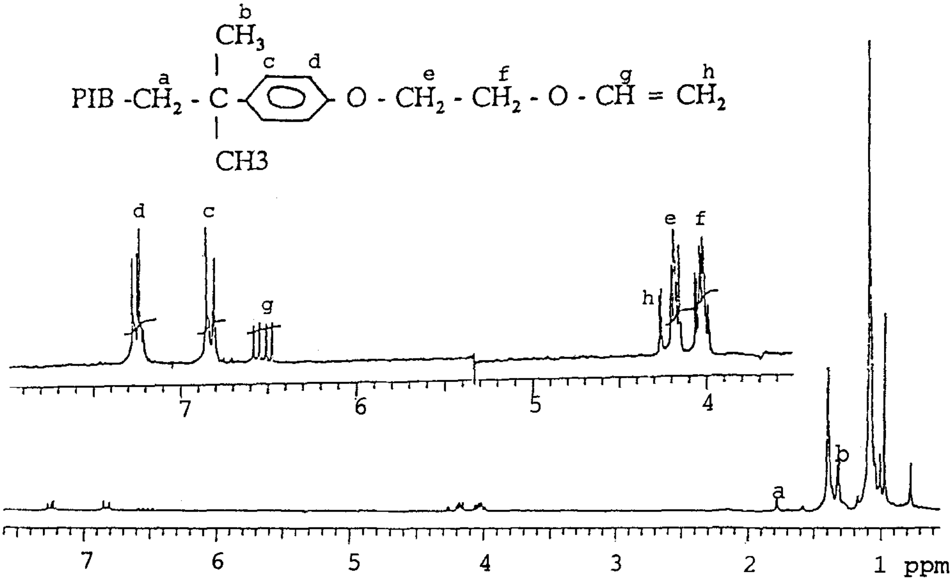


Figure 5b. ^{1}H NMR spectrum of a PIB$\sim$CH$_2$(CH$_3$)$_2$COCH$_2$CH$_2$OCH=CH$_2$ with assignments ($\overline{M}_n$ = 1040; $\overline{M}_w/\overline{M}_n$ = 1.13)

(rotavap). The functionalization of the phenol-ended PIB was carried out in the same manner. The structures of the final products were established by ^1H and ^{13}C NMR spectroscopy. The functionality was $\overline{F}_n = 1.00 \pm 0.05$ (see Fig. 4b and 5b). Quantitative phenolation was independently confirmed by ^{13}C NMR spectroscopy (not shown): Thus the characteristic resonance of $-\underline{C}H_2Cl$ completely disappeared ($\delta = 42$ ppm) whereas a new resonance characteristic of the $-O\underline{C}H_2\underline{C}H_2O-$ enchainment appeared ($\delta = 66.5 - 66.7$ ppm).

III. Results and Discussion

Figures 1a and 1b show the ^1H and ^{13}C NMR spectra of 2,2-dimethyl-4-methylene-heptyl vinyl ether. Figures 4a and 5a show the ^1H NMR spectra of the phenolated TMP and that after reaction with 2-chloroethyl vinyl ether. The chemical shift assignments were made by comparing the ^1H and ^{13}C NMR spectra of 2-chloroethyl vinyl ether, 2,4,4-trimethyl-1-pentene and 2-chloro-2,4,4-trimethylpentane respectively. Figures 2,3 and 5b show the ^1H and ^{13}C spectra of vinyl ether terminated PIB with assignments. The methodologies used have been described (8). The number average chain end functionality in both cases was close to the theoretical value: $\overline{F}_n = 1.00 \pm 0.03$ (Fig. 3) and $\overline{F}_n = \underline{1}.00 \pm \underline{0.05}$ (Fig. 5b).

The $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ (by GPC) did not change before and after functionalization within what is considered to be experimental error.

References

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