

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

**27. Bisphenol- and Trisphenol-Polyisobutylenes**

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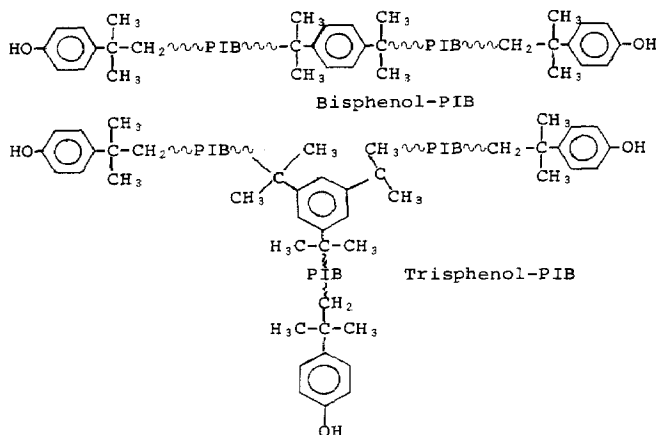
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Summary

The synthesis and quantitative end group characterization of bisphenol- and trisphenol-polyisobutylenes are described. These new telechelic prepolymers consist of a linear or a three-arm star polyisobutylene (PIB) carrying exactly two or three phenol termini, respectively. The syntheses were accomplished by quantitative Friedel-Crafts alkylation of phenol by olefin-and/or *tert.*-chlorine-telechelic PIB's and characterization involved <sup>1</sup>H NMR, UV and GPC techniques. These materials combine the chemical versatility of the -C(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OH end group with the attractive physical-chemical properties of the rubbery PIB chain.

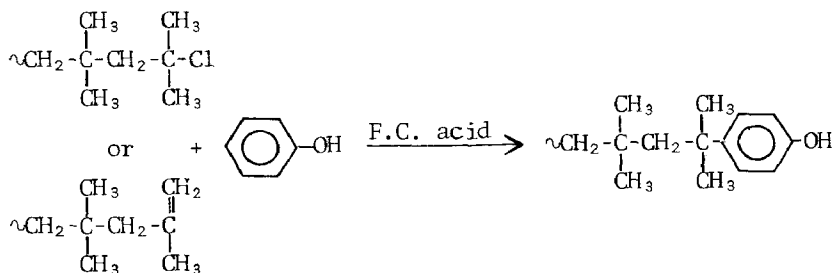
Introduction

Bisphenol-A (BPA) and related chemicals are most versatile intermediates for the preparation of numerous engineering plastics, e.g., polycarbonates, polysulfones, epoxy resins. In the course of our systematic exploration of new telechelic liquids, in particular telechelic polyisobutylene (PIB), we postulated that structures very similar to BPA could be obtained from telechelic PIB's i.e., that we could prepare linear and three-arm star PIB's carrying phenol end groups:



To emphasize the structural similarity between bisphenol-A and these PIB derivatives, we propose to call these novel telechelic materials "Bisphenol-PIB" and "Trisphenol-PIB". These structures combine the chemical versatility of the phenol terminus with the attractive physical-chemical-mechanical properties of the saturated elastomeric PIB chain and represent most interesting intermediates for the preparation of numerous useful materials. For example, bisphenol-PIB can be readily converted with epichlorohydrin to the corresponding glycidyl ether derivative (see the subsequent publication in this series), which in turn can be cured with conventional curatives (e.g., amines) employed to "harden" epoxy prepolymers. In contrast to conventional epoxy resins that tend to be brittle, these bisphenol-PIB based epoxies would be expected to be inherently flexible on account of the built-in rubbery PIB segments.

We envisioned the preparation of bisphenol-PIB and trisphenol-PIB by quantitative Friedel-Crafts alkylation of phenol by chlorine- or olefin-telechelic PIB's (F.C. acid =  $\text{AlCl}_3$ ,  $\text{BF}_3$ , etc.):



The starting materials i.e., linear and/or three-arm star chlorine- or olefin-telechelic PIB's carrying exactly two or three functional termini ( $\bar{F}_n=2.0$  and  $3.0$ ) are readily available by the inifer technique (1). The synthetic challenge resided in the developing of conditions under which alkylation of phenol was quantitative.

This paper describes the synthesis and characterization of bisphenol-PIB and trisphenol-PIB, and points the way toward the preparation of numerous novel materials containing rubbery PIB segments.

## Experimental

### Materials and Instruments

Phenol (Mallinckrodt, Analytical Reagent) was sublimed before use. Boron trifluoride etherate (Eastman) was distilled under reduced pressure. Hexanes (Fisher, Reagent) was freed from olefinic impurities by treatment with fuming sulfuric acid. 2,4,4-Trimethyl-1-pentene TMP (Phillips Petroleum, 99 mole% minimum) and cyclohexane (Fisher, Spectranalyzed) were used as received. 2-Chloro-2,4,4-trimethyl-1-pentane CIMP was prepared by hydrochlorinating TMP in  $\text{CH}_2\text{Cl}_2$  at  $\sim 5^\circ\text{C}$ .

The preparation and purification of telechelic polyisobutylenes with 2.0 or 3.0 vinylidene or tertiary chlorine end

groups have been described (1-3).

Molecular weights were determined by a Knauer Vapor Pressure Osmometer in toluene at 40°C. Absorbances were measured by a Perkin Elmer 559A UV/VIS Spectrometer. Proton NMR spectra were recorded by Varian T-60 Spectrophotometer. Gel permeation chromatography was carried out by a Waters high pressure GPC instrument using a series of five micro Styragel columns, Model 6000 pump and RI/UV dual detectors. The calibration curve was prepared by well fractionated PIB samples.

#### Alkylation of Phenol with Model Compound and Telechelic PIB Prepolymers

A representative experiment was performed as follows:

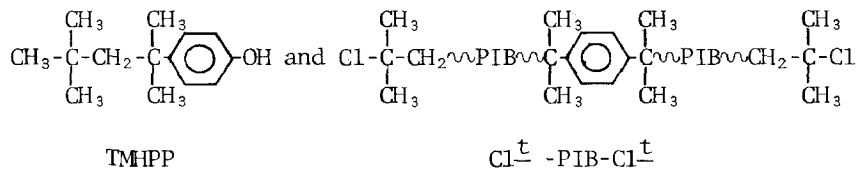
To a solution of phenol, 1 molar in hexanes, at 40-45°C stirred in a three-neck flask fitted with condenser, pressure-equalized dropping funnels, magnetic stirrer and dry-nitrogen inlet-outlet, was added freshly distilled undiluted boron trifluoride etherate (0.07 mole). Subsequently olefin or tert.-chloride (0.2 molar in hexanes) was added dropwise: The olefins used were the model compound TMP, or the olefin-telechelic PIB; the tert.-chlorides used were CTMP, or the tert.-chlorine-telechelic PIB. The olefin end group concentration of the olefin-telechelic PIB was determined by <sup>1</sup>H NMR (2) and it was assumed that the precursor, i.e., the tert.-chlorine-telechelic PIB, contained the same concentration of end groups. After the addition was complete (8-10 hours) the temperature was raised to 50-55°C and stirring was continued for ~30 hours. It was observed that with more than 10% of the catalyst based on the total quantity of phenol and at a relatively high temperature, i.e., at ~60°C, cracking of TMP occurred and p-tert.-butyl phenol was obtained. The reactor was cooled at room temperature and the brown oily layer (if any) was removed. Approximately 200 ml water were slowly added and the content of the flask was transferred to a separatory funnel. The aqueous layer was removed and the organic layer washed 8-10 times with hot water (40-50°C) followed by washing repeatedly with 50% aqueous solution of methanol. The methanol was removed by washing with cold water. Great care must be taken to remove even traces of free phenol. The presence of phenol in the washing water was monitored by UV spectroscopy. Washing was continued until the aqueous and the organic layers were free of phenol (GPC technique, UV detector). The organic layer was washed with 0.1N HCl. The acid was removed by further washings and the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>; finally the solvent was removed by rotary evaporation and the product was dried at 60°C under vacuum.

Specifically, the 2,4,4-trimethyl-2-(p-hydroxyphenyl)-pentane TMHPP model compound was prepared by alkylating phenol with either TMP or CTMP under mild conditions (see above) and recrystallizing the product three times from a n-hexane / ethanol

(95/5 v/v) mixture;  $M_p=71-72^\circ\text{C}$  (*p.tert.*-butyl phenol  $M_p=96-97^\circ\text{C}$ ).

#### Quantitative End Group (Phenol) Analysis

The  $-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{OH}$  end group concentration of bisphenol- and trisphenol-PIB has been routinely determined by UV spectroscopy combined with molecular weight (VPO) measurement. Figure 1 shows the calibration curves used for UV spectroscopy at 210 nm. For calibration purposes the bisphenol-PIB (or trisphenol-PIB) was simulated by stoichiometric mixtures of TMHPP and chlorine-telechelic PIB:



The extinction coefficients  $\epsilon$  of TMHPP and Cl<sup>t</sup>-PIB-Cl<sup>t</sup> were 14,000 and 9,600 l/mole. cm, respectively, in cyclohexane. The overall error of end group determination is  $\pm 5$  to 10%.

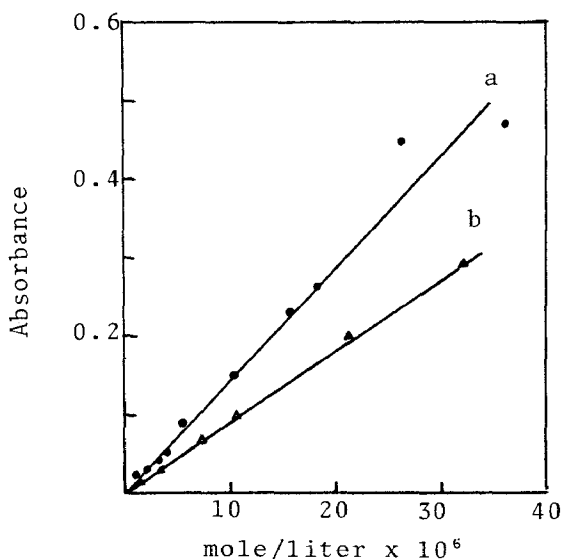


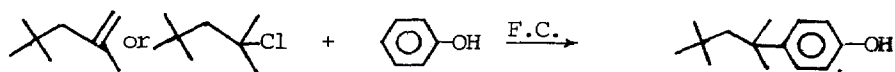
Figure 1. UV Calibration Curves of a) 2,4,4-trimethyl-2(*p*-hydroxyphenyl)-pentane, and b) Chlorine Telechelic PIB, at 210 nm

#### Results and Discussion

In order to obtain high quality networks and engineering materials from telechelic oligomers the number of functional end groups in the prepolymers must be close to theoretical. Thus

considerable effort has been devoted to the quantitative analysis of phenol end group concentration and to demonstrate that the number of phenol termini in bisphenol-PIB and trisphenol-PIB were in fact 2.0 and 3.0, respectively.

While the Friedel-Crafts alkylation of phenol with macromolecular vinylidene compounds  $\text{-CH}_2\text{=C(CH}_3\text{)-R}$  and tertiary chlorides was expected to proceed to high yield, we did not find specific literature sources claiming quantitative conversions. Thus our first task was to develop suitable experimental conditions for the quantitative alkylation of phenol by our telechelic PIB prepolymers. The first phase of these studies involved model experiments in which phenol was alkylated by TMP (a model for olefin-telechelic PIB) and CTMP (a model for chlorine-telechelic PIB) in the presence of various Friedel-Crafts acids:



After considerable experimentation we found that 100% alkylation could be achieved by both models.

Guided by the results of model experiments, phenol was alkylated by olefin- and chlorine-telechelic PIB's. The preparation of  $\text{-CH}_2\text{-C(CH}_3\text{)=CH}_2$  and  $\text{-CH}_2\text{-C(CH}_3\text{)}_2\text{Cl}$  ended PIB's has been described (1,2). The products were analyzed by  $^1\text{H}$  NMR, UV, and GPC techniques.

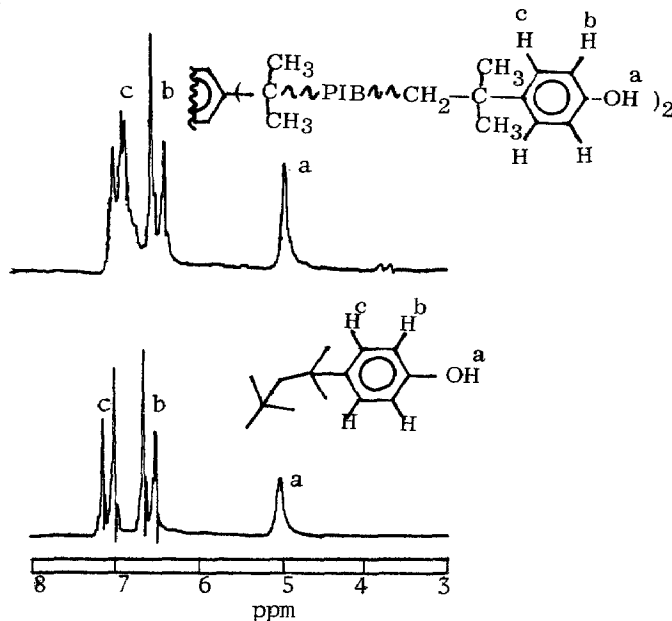


Figure 2.  $^1\text{H}$  NMR Spectra of TMHPP Model Compound and Bisphenol-PIB

Figures 2 and 3 show the  $^1\text{H-NMR}$  spectra of the model compound TMHPP, bisphenol-PIB and three-arm star olefin-telechelic-PIB and trisphenol-PIB respectively. The key resonances at 5.02, 6.72 and 7.20 ppm appearing in the model are associated with the protons of the -OH group, and of the ortho and meta positions to it, respectively; these resonances are also present at the phenol capped polymers at 5.08, 6.70 and 7.17 ppm and indicate the presence of  $\text{-C}_6\text{H}_4\text{-OH}$  end groups in the latter. Comparison of  $^1\text{H NMR}$  spectra of the authentic compounds 4-*tert.*-butyl phenol, 2-*tert.*-butyl phenol (4) with our model compound TMHPP on the one hand and bisphenol-PIB on the other hand, suggests that alkylation of phenol occurred exclusively in the *p*-position.

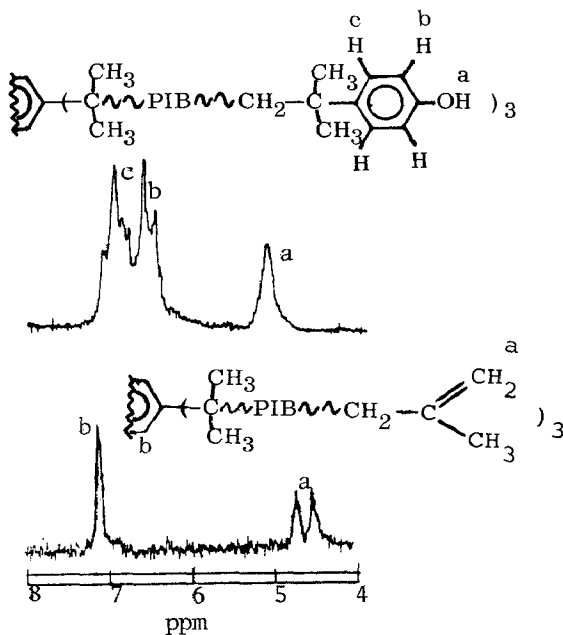


Figure 3.  $^1\text{H NMR}$  Spectra of Tri-Arm Star Olefin-Telechelic-PIB Precursor and Trisphenol-PIB

The number of phenol termini,  $\bar{F}_n$ , in bisphenol-PIB and trisphenol-PIB has been determined by UV spectroscopy combined with molecular weight determination (see Experimental). According to the data collected in Table I bisphenol-PIB and trisphenol-PIB contain 2.0 and 3.0 phenol end groups, within experimental error.

TABLE I  
 Synthesis and Characterization of  
 Bis- and Trisphenol PIB

Starting Material	Product		
	$\bar{M}_n$	$\bar{F}_n$	Phenol Functionality
$(\text{CH}_3)_3\text{CCH}_2-\text{C}(\text{CH}_3)=\text{CH}_2$	(112)	1.00	1.00
$\text{CH}_2=(\text{CH}_3)\text{CCH}_2-\text{PIB}-\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	1900	2.01	2.08
$\text{CH}_2=(\text{CH}_3)\text{CCH}_2-\text{PIB}-\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	3000	1.98	1.93
$\text{CH}_2=(\text{CH}_3)\text{CCH}_2-\text{PIB}-\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	11000	1.94	1.90
$\text{CH}_2=(\text{CH}_3)\text{CCH}_2-\underset{\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2}{\text{PIB}}$	6000	2.94	2.98
$(\text{CH}_3)_3\text{CCH}_2-\text{C}(\text{CH}_3)_2\text{Cl}$	(147)	1.00	1.00
$\text{Cl}^t-\text{PIB}-\text{Cl}^t$	1900	2.01	2.04
$\text{Cl}^t-\text{PIB}-\text{Cl}^t$	6300	1.97	2.12
$\text{Cl}^t-\text{PIB}-\underset{\text{Cl}^t}{\text{Cl}^t}$	1500	2.96	2.93
$\text{Cl}^t-\text{PIB}-\underset{\text{Cl}^t}{\text{Cl}^t}$	3500	2.90	2.91

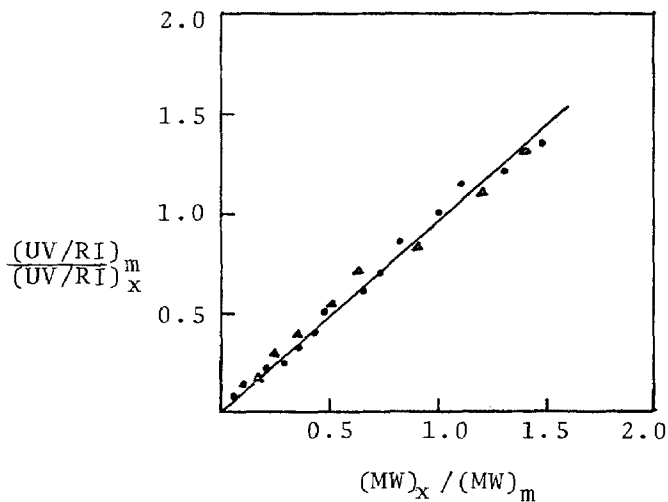


Figure 4.  $(\text{UV/RI})_m / (\text{UV/RI})_X$  versus  $(\text{MW})_X / (\text{MW})_m$  Plots for ( $\Delta$ ) Bisphenol-PIB and (o) Trisphenol-PIB

In addition to the definitive UV method described in the Experimental part the constancy of phenol end groups over the entire molecular weight distribution range has been analyzed independently by KENNEDY-SMITH plots (1). As shown by the data in Figure 4, the slopes of the linear  $(UV/RI)_m/(UV/RI)_x$  versus  $(MW)_x/(MW)_m$  plots for both bisphenol-PIB and trisphenol-PIB are within experimental error of unity (i.e., 0.92 and 0.94, respectively) indicating that the number of phenol termini remains the same in every molecular weight fraction across the entire sample.

#### References

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