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## CARBOCATIONIC POLYMERIZATION IN SUPERCRITICAL CO<sub>2</sub>. V.\* SYNTHESIS OF PHENOL-TERMINATED POLYISOBUTYLENE

György Deák<sup>\*\*\*</sup>, Tibor Pernecky and Joseph P. Kennedy<sup>\*\*</sup>

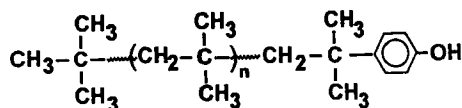
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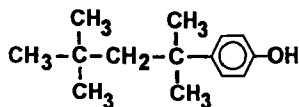
### ABSTRACT

The convenient synthesis of well-defined phenol-ended polyisobutylene (PIB):



PIB-pC<sub>8</sub>H<sub>8</sub>OH

of Mn~2000 in supercritical carbon dioxide (SC-CO<sub>2</sub>) at 140 bar and 32.5 °C has been accomplished. The synthesis involves two steps, both carried out in SC-CO<sub>2</sub>: 1. The preparation of *tert*-Cl ended PIB prepolymer (PIB-Cl<sup>†</sup>) and 2. The quantitative para alkylation of phenol by the prepolymer in the presence of BF<sub>3</sub>·OEt<sub>2</sub>. The synthesis conditions were developed by studying the model alkylation of phenol by 2-chloro-2,4,4-trimethylpentane (TMPCl) in SC-CO<sub>2</sub>, giving rise to:



TMP-pC<sub>8</sub>H<sub>8</sub>OH

\* For part IV of this series of publication, see the preceding article in this journal.

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According to quantitative  $^1\text{H-NMR}$  analysis we conclude that phenol has been quantitatively alkylated by the model compound and by the  $\text{PIB-Cl}^\ddagger$ . This is the first time electrophilic aromatic alkylations carried out in  $\text{SC-CO}_2$  solvent are described. Phenol was found to be readily soluble in  $\text{SC-CO}_2$ . Efforts to alkylate 2-bromoethylbenzene ( $\text{BrEtBz}$ ) by  $\text{PIB-Cl}^\ddagger$  in the presence of various Friedel-Crafts halides in  $\text{SC-CO}_2$  remained unsuccessful. Evidently, ill-defined side-reactions (cracking, etc.) overwhelm the desired p-alkylation at the relatively high reaction temperatures employed ( $>31^\circ\text{C}$ ).

### INTRODUCTION

The synthesis of  $\text{PIB-pC}_6\text{H}_4\text{OH}$  under conventional liquid phase conditions has been repeatedly reported [1-4]. In the course of our fundamental studies on cationic olefin polymerizations in  $\text{SCCO}_2$  [5-7], we became intrigued by the possibility of carrying out aromatic alkylation by the use of this environmentally neutral solvent and thus expand the scope of our pioneering investigations. A thorough examination of the scientific and patent literature (RAPRA, STN international, CAS data-bases until 1994) has, surprisingly, failed to indicate any prior activity in this field.

This brief communication concerns the demonstration that phenol can be quantitatively Friedel-Crafts alkylated by tert-chlorines, i.e., by  $\text{TMPCl}$  and  $\text{PIB-Cl}^\ddagger$ , in  $\text{SCCO}_2$  and that well defined phenol derivatives such as  $\text{TMP-pC}_6\text{H}_5\text{OH}$  and  $\text{PIB-pC}_6\text{H}_5\text{OH}$  can be readily prepared in this solvent system.

### EXPERIMENTAL

#### a. Materials, Equipment and Characterization Methods:

The synthesis and purification of  $\text{TMPCl}$  and the source of  $\text{BCl}_3$ ,  $\text{TiCl}_4$ ,  $\text{SnCl}_4$ ,  $\text{AlCl}_3$ ,  $\text{BF}_3\text{-OEt}_2$ ,  $\text{BrEtBz}$ ,  $\text{CH}_3\text{Cl}$  and hexanes have been described [5, 8-12]. Nitromethane (Aldrich) was distilled before use. The synthesis in  $\text{SCCO}_2$  and characterization of  $\text{PIB-Cl}^\ddagger$  ( $M_n=2000-2400$ ) was published [6].

The experiments were conducted by using a Hastelloy C pressure reactor. Details of the equipment and working conditions have been described [5, 6]. All the characterization methods have been published [5-7, 11].

#### b. Synthesis Procedures:

##### 1. Phenolation of $\text{TMPCl}$ and $\text{PIB-Cl}^\ddagger$

A 300 mL pressure reactor, equipped with a magnetic drive for the stirrer, temperature controller ( $\pm 0.1^\circ\text{C}$  control) and two sapphire windows ( $180^\circ$  apart) [5, 6] was charged at  $-50^\circ\text{C}$  in a dry-box, under dry nitrogen with 9.8 g (0.104 mole) phenol, 3 g (0.020 mole)  $\text{TMPCl}$  dissolved in 10 mL  $\text{CH}_3\text{Cl}$  and with an ampoule containing 2 mL (0.014 mole)  $\text{BF}_3\text{-OEt}_2$ . The system was heated to  $32.5^\circ\text{C}$  and pressurized with  $\text{CO}_2$  to 140 bar. Under these conditions the overall system was visibly in the supercritical state. Phenolation was started by breaking (i. e. by increasing the pressure or by activating the stirrer) the ampoule containing the  $\text{BF}_3\text{-OEt}_2$ . We believe that bulk alkylation was insignificant during the first 5-10 minutes, i.e. after the  $\text{BF}_3\text{-OEt}_2$ -containing ampoule is crushed but before reaching the final  $\text{CO}_2$  pressure (140 bar). Alkylations carried out in conventional liquid phase by the use of  $\text{BF}_3\text{-OEt}_2$  may need as much as 30-38 hours reaction time [4]. The  $\text{PIB-Cl}^\ddagger$  ( $M_n=2000$ ) is visibly soluble in the system (containing 3 v%  $\text{MeCl}$  and 3 m/v% phenol). According to continuous observations the charge remained homogeneous during the experiment. After 24 hours the reactor was cooled to  $-0^\circ\text{C}$  and slowly depressurized. The released  $\text{CO}_2$  was passed through

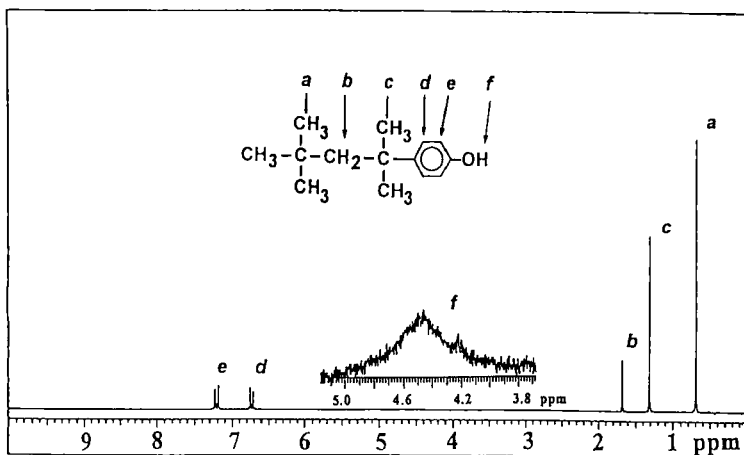


Figure 1.

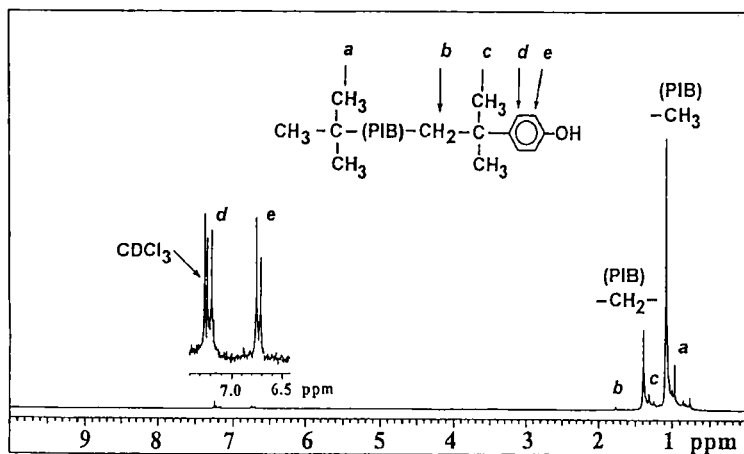
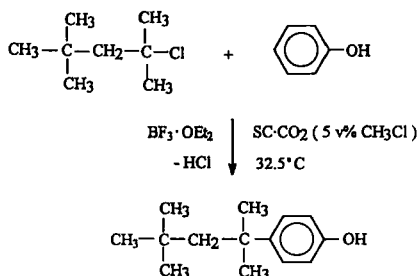
<sup>1</sup>H-NMR spectrum of TMP-pC<sub>6</sub>H<sub>4</sub>OH

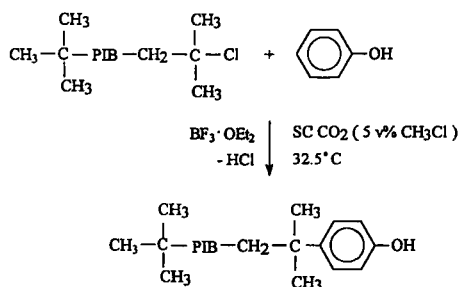
Figure 2.

<sup>1</sup>H-NMR spectrum of PIB-pC<sub>6</sub>H<sub>4</sub>OH

## I. Model reaction



## II. Alkylation of phenol



Scheme 1

Reagents, Condition, Structures

a trap at  $-50^\circ\text{C}$  to recover any dissolved product which may flash off with the released  $\text{CO}_2$ . The reactor content was dissolved in hexanes, extracted with distilled water until neutral (at least 6-7 times to remove unreacted phenol). The hexanes solution was dried over  $\text{CaCl}_2$ , filtered, and the solvent was removed at  $-0^\circ\text{C}$  by rotavap. Yield in respect to  $\text{TMPCl}$ : 3.2 g ( $\sim 75\%$ ) p(2,2,4-trimethylpentyl)phenol. The product was analyzed by  $^1\text{H-NMR}$  spectroscopy and it showed the presence of only the expected product.

The reaction with  $\text{PIB-Cl}^{\text{I}}$  was carried out in the same manner by the use of 1.3 g ( $\sim 6 \cdot 10^{-4}$  mole) of prepolymer. Yield in respect to  $\text{PIB-Cl}^{\text{I}}$ : 0.9 g of  $\text{PIB-pC}_8\text{H}_5\text{OH}$  ( $\sim 60\%$ ). The lower than 100% yields are due to unavoidable losses during recovery of the products from the complex-shaped metal reactor and to purification procedures. The  $^1\text{H-NMR}$  spectrum showed only the anticipated  $\text{PIB-pC}_8\text{H}_5\text{OH}$ .

2. Attempts to alkylate 2-bromoethylbenzene by  $\text{TMPCl}$  and  $\text{PIB-Cl}^{\text{I}}$ 

The pressure reactor was charged with 3 g (0.020 mole) of  $\text{TMPCl}$ , 6 mL (0.044 mole) of  $\text{BrEtBz}$ , 15-30 mL of  $\text{CH}_3\text{Cl}$  cosolvent and an ampoule containing the Friedel-Crafts catalyst. The reactor was heated to  $32.5^\circ\text{C}$ , pressurized with  $\text{CO}_2$  to 140 bar and the reaction was started by breaking the ampoule by increasing

TABLE 1  
 Conditions for the Attempted Alkylation of BrEtBz in SC-CO<sub>2</sub>  
 ([BrEtBz] = 37 mmole, 5v% CH<sub>2</sub>Cl, 300 mL, 32.5 °C, 140 bar)

Friedel-Crafts acid [mmole]	Alkylating Agent [mmole]	Time [hr]	Results
BF <sub>3</sub> ·OEt <sub>2</sub> [14]	TMPCl [20]	20	No reaction
BF <sub>3</sub> ·OEt <sub>2</sub> + BCl <sub>3</sub> [28+26]	TMPCl [20]	24	No reaction
AlCl <sub>3</sub> [6] <sup>a</sup>	TMPCl [17]	3	<sup>b</sup>
AlCl <sub>3</sub> [6] <sup>a</sup>	PIB-Cl <sup>†</sup> [0.5]	3	<sup>c</sup>
AlCl <sub>3</sub> + BCl <sub>3</sub> [6+52] <sup>a</sup>	PIB-Cl <sup>†</sup> [0.5]	3	<sup>c</sup>
AlCl <sub>3</sub> + CH <sub>3</sub> NO <sub>2</sub> [6+52]	TMPCl [20]	19	<sup>b</sup>
SnCl <sub>4</sub> [10]	PIB-Cl <sup>†</sup> [0.5]	22	<sup>d</sup>
TiCl <sub>4</sub> [10]	PIB-Cl <sup>†</sup> [0.5]	24	<sup>d</sup>

- <sup>a</sup>) 10 v% CH<sub>2</sub>Cl  
<sup>b</sup>) Brown oil; mainly tBu-benzenes by cracking.  
<sup>c</sup>) Depolymerization, degradation lead to mixtures of alkylated BrEtBz.  
<sup>d</sup>) Dehydrochlorination, depolymerization; no alkylation.

the pressure or by activating the stirrer. After a desired reaction time (3-24 hours) the reactor was cooled to -0 °C and slowly depressurized. The reactor content was dissolved in 100 mL hexanes and extracted with distilled water until neutral. The hexanes solution was dried over CaCl<sub>2</sub>, filtered and, the solvent and the unreacted starting materials were removed under vacuum by a rotovap. The structure of the products was analyzed by <sup>1</sup>H-NMR spectroscopy. The same procedure was also used for the attempted alkylation of BrEtBz by PIB-Cl<sup>†</sup>.

## RESULTS AND DISCUSSION

### A) The Synthesis of TMP-pC<sub>6</sub>H<sub>4</sub>OH and PIB-pC<sub>6</sub>H<sub>4</sub>OH

Figures 1 and 2 show the <sup>1</sup>H-NMR spectra of TMP-pC<sub>6</sub>H<sub>4</sub>OH and PIB-pC<sub>6</sub>H<sub>4</sub>OH, together with assignments. In view of the good resolutions quantitative product analyses can be effected. Thus integration of the resonance areas due to the aromatic nucleus (2 protons, doublet at 6.8 ppm) relative to that of the -CH<sub>2</sub>-protons closest to the phenyl ring (2 protons, singlet at 1.68 ppm) yields in both cases 1 phenyl ring per alkyl substituent, i.e., the number average phenol end-functionality per molecule is close to the theoretical value, F<sub>n</sub> = 1.0 ± 0.1. We believe that ortho substitution is essentially absent or if present its contribution to the product is insignificant because the doublets at 6.8 and 7.2 ppm indicate the exclusive presence of para

substitution. The source of the shoulder at 4.2 ppm is unknown (artefacts?). The molecular weight of the PIB- $p\text{-C}_6\text{H}_5\text{OH}$  was determined both by  $^1\text{H-NMR}$  spectroscopy and GPC, and the values were in good agreement:  $M_n = 2200$  and  $2400$ , respectively. Scheme 1 outlines the reagents, conditions and structures obtained.

Alkylation of phenol by TMPCl in the presence of  $\text{BF}_3\cdot\text{OEt}_2$  in hexanes solvent at  $-60^\circ\text{C}$  yields *p-tert*-butylphenol because of cracking of TMPCl under Friedel-Crafts conditions [4]. Interestingly, in  $\text{SCCO}_2$ , under similar conditions extensive cracking must have been absent because in both the TMPCl and PIB- $\text{Cl}^\ddagger$  experiments the corresponding  $^1\text{H-NMR}$  spectra did not indicate the presence of *p-tert*-butylphenol.

#### B) Attempted Synthesis of PIB- $p\text{-C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br}$

In view of our success in the synthesis of phenol derivatives under very mild conditions, attempts have been made to alkylate BrEtBz by PIB- $\text{Cl}^\ddagger$ , and thus to prepare PIB- $p\text{-C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br}$  a precursor of styryl-ended PIB [12]. Despite of repeated trials by the use of various Friedel-Crafts acids under a variety of conditions, a satisfactory procedure for the synthesis of this product could not be developed.

Table 1 summarizes the conditions tried and outlines the results. Under the mild conditions alkylation by TMPCl of phenol occurs readily, BrEtBz cannot be alkylated, even in the presence of  $\text{BCl}_3$  (rows 1 and 2, Table 1). The use of TMPCl and/or PIB- $\text{Cl}^\ddagger$  in conjunction with the relatively strong Friedel-Crafts acid  $\text{AlCl}_3$  under various conditions (rows 3-6) induces side reactions (cracking, depolymerization) which lead to ill-defined mixtures of products. PIB- $\text{Cl}^\ddagger$  in the presence of  $\text{SnCl}_4$  or  $\text{TiCl}_4$  (rows 7, 8) does not alkylate BrEtBz even after a day, rather it undergoes dehydrochlorination and depolymerization.

#### ACKNOWLEDGEMENT

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