# Polymerization of 1-Bromo-4-lithiobenzene in THF. A Route to Soluble Polyphenylenes

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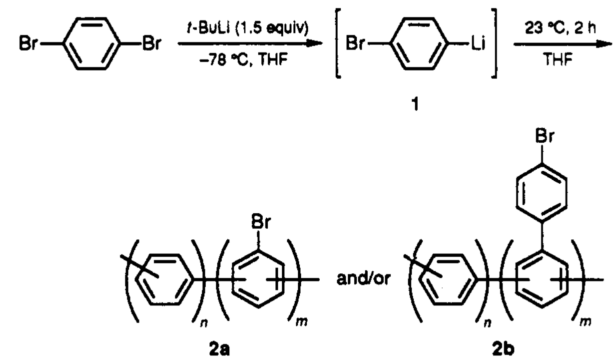
Polyphenylene exhibits a number of diverse properties that have prompted its use in numerous composite materials including insulating layers for semiconductors, doped electrical conductors, metal catalyst supports, and lubricant additives. While poly(*p*-phenylene) (PPP) is intractable even with degrees of polymerization of 10–15, the presence of ortho or meta linkages destroys the crystallinity to such an extent that soluble material can be formed.[2]

We recently described a method for the formation of 1-bromo-4-lithiobenzene (1) by the treatment of *p*-dibromobenzene with *tert*-butyllithium in 1,4-dioxane. Compound 1 could be instantaneously polymerized, even at −78 °C, by the addition of hexamethylphosphoramide (HMPA) to afford brominated polyphenylene.[3] The FTIR absorption intensity for the para linkage was 3–4 times more intense than the non-para-linked intensities. It was the presence of the non para linkages or phenylated units that caused the crystallinity to be destroyed, rendering polymers that were soluble even with degrees of polymerization over 40 (SEC relative to polystyrene). Here we describe the polymerization of 1 in THF without the need for the highly toxic cancer suspect agent HMPA.

The polymerization procedure is as follows. To a solution of *p*-dibromobenzene (16 mmol) in THF (16 mL) at −78 °C was slowly added *tert*-butyllithium (24 mmol, 2.3 M in pentane). Note that 12 mmol of *tert*-butyllithium were utilized for the lithium–halogen exchange and 12 mmol were consumed for the elimination of the *tert*-butyl bromide to afford lithium bromide, isobutylene, and isobutane. Thus the use of *tert*-butyllithium allowed all the byproducts to be innocuous, i.e., no alkyl halides remained in solution. Accordingly, 4 mmol of *p*-dibromobenzene remained unreacted. If we used 2.0 equiv of *tert*-butyllithium to convert all of the *p*-dibromobenzene to 1, significantly lower yields (26%) of the final ether-insoluble polymer were obtained. This may be due to the formation of small amounts of *p*-dilithiobenzene, a possible chain-termination agent. The intermediacy of 1 at −78 °C was confirmed in a separate experiment by the addition of chlorotrimethylsilane (TMSCl) at that temperature to form 1-bromo-4-(trimethylsilyl)benzene. Upon complete addition of the *tert*-butyllithium, the solution was allowed to warm to room temperature and stirred for 2 h. Quenching with water and isolation of the ether-insoluble portion afforded 0.79 g (65%)[4] of **2** (**2** could be either **2a** or **2b** or a mixture of both) that was freely soluble in THF, $CH_2Cl_2$, and $CHCl_3$ (eq 1). The polymer prepared in this manner had approximately one bromide for every three aryl groups by elemental analysis.[4] We have screened several solvents (THF, ether, 1,4-dioxane, and DME), polymerization temperatures (−78 to +60 °C), polymerization times (5 min to 2 days), and *tert*-butyllithium amounts (1.0–2.0 equiv), but the conditions described above afforded the highest yields (60–65%) and highest weight-average molecular weights of the ether-insoluble fraction.




(1)

By the FTIR analysis of **2**, there were approximately equal intensity bands for para-linked (810 $cm^{-1}$) and meta-linked (889 and 787 $cm^{-1}$) absorbances.[5] The previous HMPA-promoted method gave a significantly more intense para-linked absorbance. Additionally, the overtone band at 1900 $cm^{-1}$ was also attributed to the para-substituted units while the C–Br stretch was evident at 1074 $cm^{-1}$.[2i,j] Disubstituted ortho-linked units should give a band at 750–755 $cm^{-1}$.[6] Though we see no clearly distinguishable band in the 750–755-$cm^{-1}$ region, a shoulder on the low wave number side of the 787-$cm^{-1}$ meta band may be attributed to an ortho-substituted pattern. Since phenylated polyphenylenes show both ortho and para absorbances, and they are soluble materials, we may have phenylated polyphenylene units as in **2b**.[2w,6] Though powder X-ray diffraction (XRD) signals have been reported for PPP,[2b,i] no diffraction pattern was observed for **2**, consistent with the solubility of the material. Likewise, scanning electron microscopic (SEM) analysis showed a globular morphology pattern. Size-exclusion chromatography (SEC) showed that **2** had a 6:4 bimodal distribution with $M_w$ = 1944 and $M_w/M_n$ = 3.89 relative to polystyrene. There was no aliphatic material present in the polymer by $^1H$ NMR (500 MHz, $CDCl_3$) with the aromatic signal at $\delta$ 7.2–7.9. The $^{13}C$ NMR (125 MHz, $CDCl_3$) spectrum showed peaks in the range $\delta$ 124–135 and a smaller set at $\delta$ 139–141.[7] The UV–visible absorption maximum was observed at 284 nm ($CHCl_3$), consistent with mixtures of para and meta/ortho linkages since the absorption maxima for *p*-sexiphenyl and *m*-sexiphenyl are 318 and 248 nm, respectively.[8] Thermogravimetric analysis (TGA; $N_2$, 20 °C/min) of the brominated polymer **2** showed a 10% weight loss at 385 °C and a total weight loss of 48% at 900 °C. Differential scanning calorimetry (DSC; $N_2$, 20 °C/min) showed melting events at 152 and 175 °C with a sharp exotherm at 410 °C.

Removal of the bromides from the polymer was achieved by simple lithium–halogen exchange with *tert*-butyllithium and quenching with water to form the debrominated material **3**.[3] The FTIR terminal phenyl stretch increases substantially (758 and 697 $cm^{-1}$), suggesting the presence of phenylated polyphenylene that was previously capped with bromides at the para position as in **2b**. No C–Br stretch was detected in the debrominated material. Interestingly, when a sample of **2** having $M_w$ = 1873 ($M_w/M_n$ = 2.83) by SEC was debrominated, the value of $M_w$ increased to 2323 ($M_w/M_n$ = 2.68). We observed this pattern previously with the HMPA-promoted reaction.[3] SEC is a measure of the hydrodynamic volume and not a direct measure of the molecular weight. Hence, it could be an effect of the bromides on interaction with the column packing material (cross-linked polystyrene). However, when the debromination was carried out in the presence of HMPA, the percentage increase in $M_w$ was significantly greater ($M_w$ = 1970, $M_w/M_n$ = 3.11, increased to $M_w$ = 2773, $M_w/M_n$ = 3.41). This certainly implies that the mo-

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lecular weight is increasing on debromination and even further on debromination in the presence of HMPA. It is not just an effect of the bromides causing elution retardation on chromatography. $^1$H NMR (300 MHz, $CDCl_3$) showed no aliphatic material with aromatic signals at $\delta$ 7.0–7.9. $^{13}$C NMR (75 MHz, $CDCl_3$) showed a large set of signals at $\delta$ 126–131 and a smaller set at $\delta$ 139–142 for the tetrasubstituted carbons. The UV–visible absorption maximum was at 288 nm ($CHCl_3$). TGA ($N_2$, 20 °C/min) of **3** showed a 10% loss at 429 °C and a total loss of 52% at 900 °C. Remarkably, the total weight loss of the brominated polymer **2** was very similar to that of the debrominated polymer **3**. DSC ($N_2$, 20 °C/min) analysis of the debrominated polymer showed a gradual endotherm in the range 170–230 °C with another large endotherm at 410 °C.

There were several interesting observations concerning the polymerization process that should be noted. First, after stirring the polymerization solution at room temperature for 2 h as described above, we noticed rapid evolution of a gas upon quenching with water. The gas was shown to be $H_2$ by mass spectrometric (MS) analysis. When we quenched the reaction mixture with $D_2O$, then DH was detected. No $D_2$ was present, confirming the absence of Li(0) in the reaction mixture. Surprisingly, however, on quenching with $D_2O$, the amount of DH to $H_2$ formed was 1:1.4. This was checked several times with different sources of $D_2O$ with a deuterium content >99%. This may be from a large isotope effect, but this observation is being investigated more fully. Presumably, the source of the $H_2$ on quenching was from the reaction of the water with LiH. The LiH could be formed by elimination from a lithiated aromatic to form an ortho benzyne intermediate. Quantitation of the $H_2$ evolution showed approximately 1.9–2.3 mmol of $H_2$ formation/10.0 mmol of **1**. In order to further probe the mechanism of the polymerization, we quenched the reaction mixture with TMSCl rather than water. Surprisingly, by $^1$H NMR analysis, no silylated material could be detected in any of the isolated material whether ether soluble or ether insoluble. Hence, the polymer does not exist as the polylithiated system and there does not even appear to be a lithiated end to the polymer. The results of the $H_2$ formation and the lack of any silylated polymer on quenching with TMSCl are quite intriguing; however, we are not yet able to propose a mechanism that is consistent with all of the observations, namely, mixtures of para, meta, and possibly some ortho linkages, high bromide content in the polymer, no lithiated residues on the prequenched polymer, and generation of lithium hydride. There is the possibility of an aryne process involving both para benzyne[9] and ortho benzyne[10] formation. Additionally, an $S_{RN}1$ mechanism may be in operation.[11]

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**Supplementary Material Available:** Spectral, thermal, and chromatographic plots for compounds **2** and **3** (16 pages). Ordering information is given on any current masthead page.

## References and Notes


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(4) Calculated elemental data for one Br per three aryl units. Calcd for $C_{18}H_{11}Br$: C, 70.36; H, 3.58; Br, 26.06. Found: C, 71.49; H, 4.15; Br, 24.33. Based on $C_{18}H_{11}Br$ for three aryl units, the average MW of a monomer unit is 307/3 = 102. The limiting reagent in the reaction is *tert*-butyllithium at 12 mmol; hence, the reaction yield is ~65%.

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