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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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**To cite this Article** Dhal, Pradeep K.(1992) 'Facile Synthesis of 4-Bromo-4'-Vinyl Biphenyl and Its Polymerization: A Preliminary Study', Journal of Macromolecular Science, Part A, 29: 1, 39 – 45

**To link to this Article: DOI:** 10.1080/10101329208054562

**URL:** <http://dx.doi.org/10.1080/10101329208054562>

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## FACILE SYNTHESIS OF 4-BROMO-4'-VINYL BIPHENYL AND ITS POLYMERIZATION: A PRELIMINARY STUDY

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### ABSTRACT

4-Bromo-4'-vinyl biphenyl, a reactive functional monomer was synthesized in satisfactory yield through a convenient procedure. This monomer readily polymerized offering a powdery polymer which is soluble in a number of organic solvents. The molecular and spectroscopic properties of the polymer were investigated. Preliminary experiments with respect to the reactivity of the bromophenyl residues suggest that they are highly accessible to chemical reagents.

### INTRODUCTION

Ever since Merrifield demonstrated the utility of polymeric supports for solid-phase peptide synthesis (1), reactive functional polymers are finding increasing applications in the areas of organic synthesis, catalysis, separation science, biotechnology etc (2). This has given rise to widespread research interests in developing newer and efficient synthetic routes for obtaining functional polymers. While there exist two different approaches for functional polymer synthesis, viz. (i) synthesis of functional monomers and their subsequent polymerization and (ii) chemical modification of premade polymers, the later approach has attracted more attention. The superiority of chemical modification approach stems from the fact that the structure and composition of the parent polymer remain unchanged and the versatility of different polymer analog chemical reactions enables to introduce large varieties of functional groups. In this regard poly (4-bromo styrene) has been on the focus for some time, as it provides ample scope for introducing different types of functional groups (3).

Studies have been directed in recent time to improve the performance of these polymer matrices by increasing the accessibility of the functional groups and the thermo-mechanical stability of the matrix resin for enhancing their applications under extreme conditions. Towards this end, attempts have been made to introduce spacer concept, rigid monomer/polymer systems *etc* (4).

Polymers based on 4-bromo-4'-vinyl biphenyl (BVB) appear to be interesting from the view point that for chemical reactions they provide the similar reactive sites as poly (4-bromo styrene). In addition, the functional group is more accessible in this case due its farther location from the polymer backbone. Yet, it provides better

thermomechanical stability to the polymer matrix due to the presence of rigid biphenyl moieties. Taking all these aspects into consideration, a convenient route for synthesizing this monomer and its polymerization has been developed. The present communication is restricted to the synthesis of the monomer, its polymerization and molecular characterization. The details on its copolymerization and chemical modifications will be published in future.

## EXPERIMENTAL

**Materials:** All the reagents were of analytical grade obtained from Fluka AG and were used as received. All the solvents were reagent grade and were subjected to standard methods of purification prior to their use.

**Synthesis of the Monomer:** The synthetic route adopted for this monomer synthesis (Scheme I) consists of two steps *viz.* (i) synthesis of 4-bromo-4'-formyl biphenyl (2) and (ii) synthesis of BVB (3).

**(i) 4-Bromo-4'-Formyl Biphenyl (2):** Under dry nitrogen, 17.56 g (0.93 mmol) of  $\text{TiCl}_4$  was added to a stirred solution of 10 g (0.43 mmol) of 4-bromo biphenyl (5) dissolved in 50 ml of absolute dichloromethane. The temperature was maintained at  $0^\circ\text{C}$ . To this mixture 6g (0.53 mmol) of dichloromethyl methyl ether was added dropwise. The reaction mixture was slowly warmed up to room temperature and stirred at this temperature for 24 hrs. The mixture was then slowly poured into 500 ml of ice cold water with rapid stirring. The reaction mixture was extracted with diethyl ether (3x100 ml) and dried over anhydrous sodium sulfate. The solvent was subsequently removed under vacuum and the residue was flash chromatographed with silica gel using benzene as eluent. The product was finally crystallized from ethanol to give 9.2g (Yield 82%) of 2: m.p.  $131-132.5^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) in ppm: 7.5-7.8 (8H, m, aromatic) and 10.6 (1H, s, CHO); Anal Calc for  $\text{C}_{13}\text{H}_9\text{BrO}$ : C, 59.79; H, 3.47. Found C, 59.53; H, 3.56.

**4-Bromo-4'-Vinyl Biphenyl (3):** Under dry nitrogen atmosphere, a suspension of 3.15g (28 mmol) of potassium tert. butoxide, 10.1g (28 mmol) of methyltriphenyl phosphonium bromide and 200 mg of 18-crown-6 in 75 ml of absolute THF was cooled to  $0^\circ\text{C}$ . While stirring, 6.71g (25.6 mmol) of 2 in 20 ml of absolute THF was added dropwise to this cooled suspension. The reaction mixture was stirred for additional 2 hrs at room temperature. At this time the suspension was filtered off and washed with 10 ml of THF. The combined filtrate was evaporated to dryness. The resulting residue was treated with 50 ml of dry ether, stirred for 30 minutes and filtered off. The filtrate was passed through a pad of neutral alumina and the later was washed with 20 ml of ether. The combined organic phase was evaporated to dryness and the residue was finally recrystallized from isopropanol providing 4.9g (74% yield) of 3. m.p.  $129^\circ\text{C}$  (Lit. (6)  $128^\circ\text{C}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) in ppm: 5.25-5.85 (2H, 2d, vinyl  $\text{CH}_2=\text{C}$ ); 6.65 - 6.80 (1H, 2d, vinyl  $\text{CH}=\text{C}$ ); 7.40 - 7.60 (8H, m, aromatic). Anal Calcd for  $\text{C}_{14}\text{H}_{11}\text{Br}$ : C, 64.88; H, 4.28. Found C, 64.62; H, 4.35.

**Polymerization of BVB:** The radical polymerization of BVB was carried out at  $60^\circ\text{C}$  in nitrogen atmosphere using AIBN as the free radical initiator making a 15% solution of the monomer in the appropriate solvent. After polymerizing for 2 to 3

hrs, the reaction mixture was poured into excess methanol. The polymer obtained was purified by repeated dissolution and reprecipitation from THF and methanol respectively. The polymer was subsequently dried at 50°C under reduced pressure to constant weight.

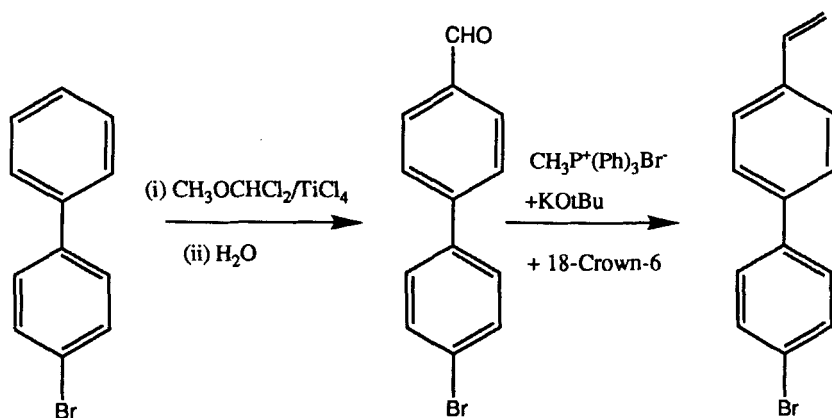
**Measurements:** The NMR spectra were recorded using Varian VXR 300 spectrometer and the chemical shifts were assigned using TMS as the internal standard. The molecular weights of the polymers were determined with a Waters Associates Model 990 liquid chromatograph fitted with  $\mu$ -Styragel column using THF as eluent and monodisperse (uniform) polystyrene as standard for universal calibration curve.

## RESULTS AND DISCUSSION

The synthesis of BVB was first reported by Kawakami et al. (6). The procedure is not quite appealing, since it involves the use of a symmetrical 4,4'-dibromo biphenyl which needed to be mono lithiated followed by ethylene oxide treatment, tosylation and elimination. The method suffers from the limitation of lack of selectivity with respect to mono lithiation and the substrate showed solubility problem which lead to overall low yield.

To overcome these difficulties, a relatively straight forward approach to synthesize this compound has been developed. The synthetic procedure as shown in scheme I consists of two steps. The first step involves the formylation of 4-bromo biphenyl followed by Wittig olefination of the resulting aldehyde. Titanium tetrachloride catalyzed Friedel-Crafts alkylation of 4-bromo biphenyl with dichloromethyl methyl ether followed by hydrolysis offered the desired aldehyde product **2** in excellent yield (82%). Use of excess of the reagent and low temperature operations are the appropriate conditions for improved yield. Spectral analysis of the product is suggestive of formylation at 4' position. the vinyl group was introduced by Wittig reaction of the aldehyde with methyltriphenyl phosphonium bromide. Amongst different bases used, potassium tert. butoxide gave the most satisfactory yield. Addition of small amount of the crown ether improved the product yield. Passage through an alumina column and subsequent recrystallization from isopropanol were efficient techniques to get rid of the triphenylphosphine oxide impurities. The compound exhibited all the desired molecular and spectral characteristics.

AIBN initiated free radical polymerization of this monomer in 1,4-dioxane gave a white powdery product showing a melting point of 262°C. The polymerization reactions were also successfully carried out in toluene, DMF and THF. The polymer was soluble in various organic solvents like chloroform, benzene, acetonitrile as well as the solvents used for its polymerization. The number average molecular weight of different polymers determined by GPC method were found to be in the range of 30,00 to 75,000. The value of  $M_n$  decreased with increasing initiator concentration. Table 1 shows the results on the polymer yield and their molecular weight for different solvent systems and initiator concentrations. The polymer was also characterized by elemental analysis, differential scanning calorimetry, infrared and NMR ( $^{13}\text{C}$  and  $^1\text{H}$ ) spectroscopy. These data were in compliance with polymer structure. The  $^{13}\text{C}$  NMR spectrum of this polymer was analyzed in greater detail to obtain information on chain structure.



Scheme 1: Synthetic approach to obtain 4-bromo-4'-vinyl biphenyl.

TABLE 1

Polymerization of 4-Bromo-4'-Vinyl Biphenyl in Different Solvents with Varying Initiator Concentrations<sup>a</sup>.

| Entry | Solvent | Wt.% of initiator<br>with respect to monomer | % Conversion | $\bar{M}_n \times 10^{-4}$ |
|-------|---------|--|--------------|----------------------------|
| 1     | Dioxane | 0.5  | 38.5         | 7.5                        |
| 2     |         | 1.1  | 45.0         | 6.2                        |
| 3     |         | 1.5  | 58.0         | 5.6                        |
| 4     | DMF     | 0.6  | 45.0         | 7.1                        |
| 5     |         | 0.9  | 60.5         | 5.8                        |
| 6     |         | 1.4  | 65.0         | 5.2                        |
| 7     | Toluene | 0.6  | 40.0         | 5.2                        |
| 8     |         | 1.1  | 82.0         | 4.3                        |
| 9     |         | 1.4  | 68.0         | 3.9                        |

a: In all cases 1 g of the monomer was polymerized by dissolving in 5 ml of the appropriate solvent

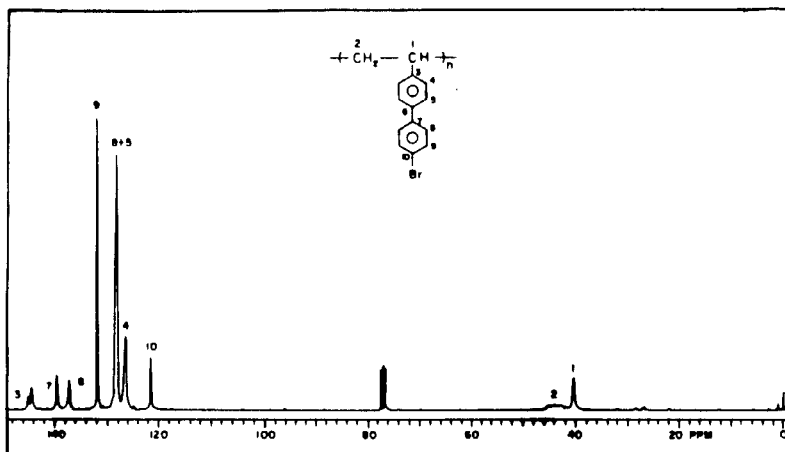


Figure 1. Proton decoupled 75 MHz  $^{13}\text{C}$  NMR spectrum of poly (4-bromo-4'-vinyl biphenyl).

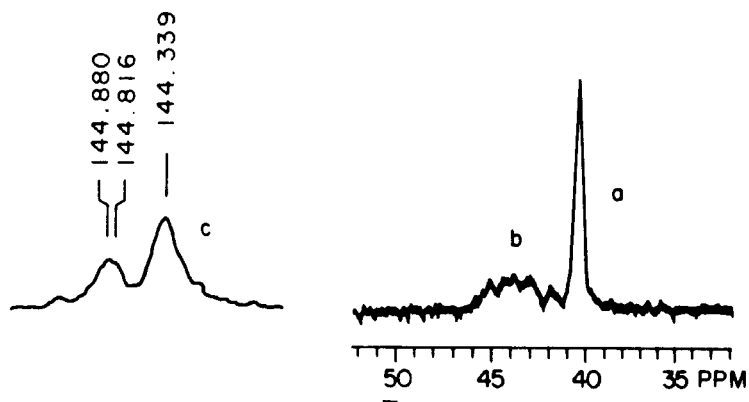


Figure 2. Expanded resonance patterns of (a) backbone methine; (b) backbone methylene and (c) aromatic C-3 carbon atoms of poly (4-bromo-4'-vinyl biphenyl).

TABLE 2

Results on the Tacticity Analysis of Poly (4-bromo-4'-vinyl biphenyl) from  $^{13}\text{C}$  NMR Data.

| Type of sequence               | $^{13}\text{C}$ Chemical shift (in ppm ) | Relative Abundance |
|--------------------------------|--|--------------------|
| Aromatic C-1 carbon atom       |  |                    |
| rr                             | 144.34                                   | 56                 |
| mr+rm                          | 144.82                                   | 36                 |
| mm                             | 145.63                                   | 8                  |
| Backbone methylene carbon atom |  |                    |
| mrm                            | 41.54                                    | 6                  |
| rrm                            |  | 28                 |
| rrr                            | 42.82                                    | 37                 |
| mmm                            | 43.76                                    | 5                  |
| mmr                            | 44.05                                    | 10                 |
| rmr                            | 44.92                                    | 13                 |

The  $^{13}\text{C}$  NMR spectrum of the polymer obtained in dioxane is depicted in Fig.1. Assignments of different signals to various carbon atoms constituting the polymer chain were performed with the help of distortionless enhancement by polarization transfer (DEPT) experiment and theoretical calculations of substituent dependent chemical shifts (7). The  $^{13}\text{C}$  resonances of interest for tacticity studies include those due to backbone methine and methylene carbon atoms and aromatic C-3 carbon atom of biphenyl ring directly linked to the polymer backbone. Presented in Fig.2 are the expanded plots of these resonances. As is evident, the backbone methine shows a single resonance line at 40.45 ppm (Fig. 2a) without any fine structure splitting, suggesting its apparent insensitivity to chain stereochemistry. On the other hand, the backbone methylene and aromatic C-3 carbon atoms show several fine structures. The methylene carbon atom resonates over 41.20 - 46.05 ppm showing five clear signals, which were conveniently used for tetrad assignment. Since the structure of this polymer is closely analogous to that of polystyrene, the signal assignments to different stereosequences were made in the light of the results reported for polystyrene (8). This has been supplemented by intensity calculations based on Bernoullian method. Both the results are in mutual good agreement and are summarized in Table 2. The aromatic C-3 carbon atom resonates over 143.90 - 146.25 ppm showing three signals assignable to triad structures. Like the previous case, in the light of polystyrene structure the three signals were assigned to be syndiotactic, heterotactic and isotactic with decreasing order of field strength. The polymer, in overall possesses a stereorandom structure with higher bias for syndiotactic placement.

With regard to chemical reactivity of the bromobiphenyl moiety, treatment of this polymer with butyl lithium followed by hydrolysis offered a product having structure identical with poly(4-vinyl biphenyl). This provides a guideline for the use of the lithiated polymer to incorporate variety of functional groups to the polymer matrix through polymer modification reactions. Work is currently under progress towards this end.

### ACKNOWLEDGEMENTS

My sincere thanks are due to Prof. G. Wulff for his supports, encouragements and helps.

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