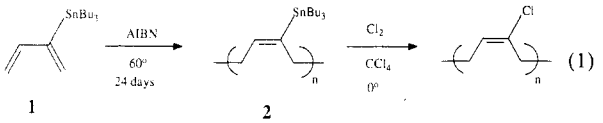
Transition-Metal-Catalyzed Modification of Polymer Backbones. 1. Palladium-Catalyzed Cross-Coupling Reactions of Copolymers Containing Vinyltributylstannane and Vinyl Iodide Groups

MICHAEL E. WRIGHT* and SHON R. PULLEY

Department of Chemistry & Biochemistry, Utah State University, Logan, Utah 84322-0300.
Received July 18, 1988

Introduction

The stereoregular polymerization of monomers results in polymeric materials that have very specific mechanical and chemical properties. The use of 2-substituted butadiene monomers usually results in a microstructure of (*E*)- and (*Z*)-1,4-polybutadiene as well as varying percentages of 1,2- and 3,4-addition products under conditions of anionic and free-radical polymerization.[1] Aufdermarsh and co-workers at Du Pont reported the first synthesis of (*E*)-polychloroprene by chlorinolysis of (*E*)-1,4-poly[2-(tributylstannyl)-1,3-butadiene] (**2**) (eq 1).[2]

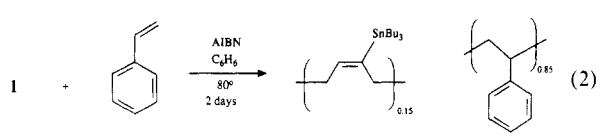


1 2 (1)

A very recent example of a stereoregular polymerization of a 1,3-butadiene derivative was accomplished by Weber and Ding via the anionic polymerization of 2-(triethylsilyl)-1,3-butadiene to give (*E*)-1,4-poly[2-(triethylsilyl)-1,3-butadiene] (**3**).[3] They found the formation of the (*E*)-1,4-microstructure to be both regio- and stereospecific on the basis of spectroscopic data.

The ultimate utility of stereoregular polymers such as **2** and **3** lies in the availability of methods to alter the vinyl functionalities in the final polymer product. Vinylstannanes[4] and vinylsilanes[5] are known to undergo electrophilic reactions leading to a variety of functionalized vinyl compounds. A very attractive feature offered by vinylstannanes is their established reactivity in palladium-catalyzed cross-coupling reactions (e.g., the Stille reaction).[6] A general procedure involves the reaction of the vinylstannane with a cross-coupling partner (e.g., ArX, RCOCl) in the presence of a catalytic amount of palladium. The reaction conditions are very mild and neutral, which allows the cross-coupling of molecules that contain sensitive functionalities.[6]

We report the free-radical copolymerization of styrene and 2-(tributylstannyl)-1,3-butadiene (**1**) to give copolymer **4** (eq 2) and the subsequent modification of the vinyltributylstannane moiety using palladium-catalyzed cross-coupling reactions. The cross-coupling methodology for the modification of the backbone appears to show good stereospecificity.



(2)

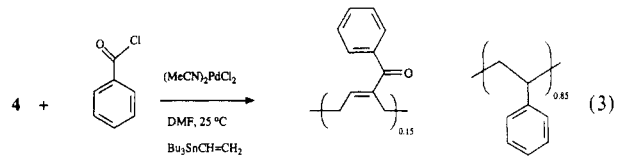
4

Results and Discussion

The free-radical copolymerization of **1** and styrene (0.20 mole ratio, respectively) affords the predominantly (*E*)-1,4-butadiene copolymer **4** in 72% isolated yield. Combustion analysis of the copolymer indicates incorporation of the tin monomer to be 15 mol %, which is supported below by subsequent reactions of the copolymer. Gel permeation chromatography (GPC) analysis of **4** shows a molecular weight distribution to be of low dispersion with M_w/M_n = 1.37 and M_w = 10052.

The predominant (*E*)-1,4-microstructure is supported by the lack of absorptions in the infrared spectrum at 980 and 910 cm^{-1}, where vinyl and terminal methylenes normally absorb.[7] Similar arguments used to assign the stereochemistry in the homopolymerization of **1** (i.e., **1** exists solely in the s-cis form) are valid for the copolymerization reaction. Furthermore, only a single resonance at δ 5.20 ppm in the ^1H NMR spectrum is observed in the vinyl region. Although the infrared and ^1H NMR spectroscopic data do not show evidence for any 3,4-addition product, there does appear to be some indication for that isomer being present (see below).

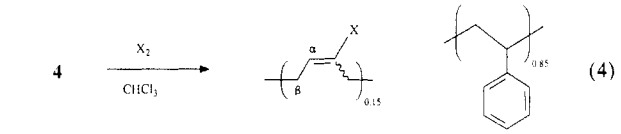
The importance of the (*E*)-1,4-microstructure can be carried over to a new method for the stereospecific modification of the polymer backbone. Vinylstannanes are known to undergo palladium-catalyzed coupling reactions with a high degree of stereospecificity.[7] Reaction of **4** with benzoyl chloride in the presence of a palladium catalyst affords the modified copolymer (eq 3). A major difficulty in the synthesis of **5** is removal of the tributylchlorostannane byproduct at the completion of the reaction. Several precipitations of the polymer in cold pentane do remove the organostannane byproduct but at the expense of lowering the yield of polymer. Treatment of an ether solution of **5** with aqueous potassium fluoride did not appear to convert the tributylchlorostannane to the insoluble fluoride derivative. The ^1H NMR spectrum of **5** displays a single vinyl proton resonance at δ 5.15 ppm, which is consistent with a stereospecific cross-coupling reaction.



5 (3)

The conditions necessary to carry out the cross-coupling reaction in the polymer are more vigorous than required in monomeric analogues. Use of the more reactive precatalyst $(CH_3CN)_2PdCl_2$ in DMF allows the reaction to proceed at lower temperatures and shorter reaction times.

Treatment of copolymer **4** with molecular iodine or bromine gives a copolymer which appears to have isomerized (eq 4) as evidenced by two vinyl CH signals in the ^1H NMR spectra. The (*E*)- and (*Z*)-vinyl CH signals of copolymer **6b** appear in the ^1H NMR at δ 4.95 and 5.90 ppm, respectively. Identical isomeric ratios are obtained when the reaction is carried out at −78 °C. Monomeric vinylstannanes are known to undergo electrophilic cleavage with I_2 with a high degree of stereospecificity;[9] therefore, some property of the copolymer must be affecting the selectivity of the reaction.



(4)

6a, X = Br
6b, X = I

Reaction of copolymer **6b** with (phenylethynyl)trimethylstannane in the presence of palladium gives complete reaction of the vinyl iodide sites (i.e., 0.0% I in **7**),

0024-9297/89/2222-2542$01.50/0

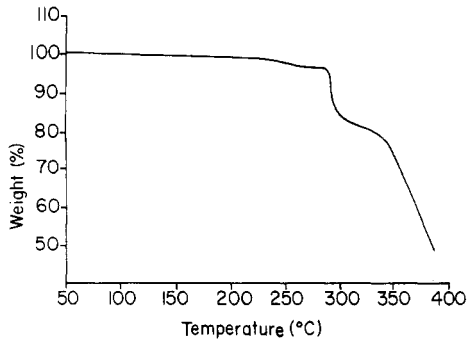
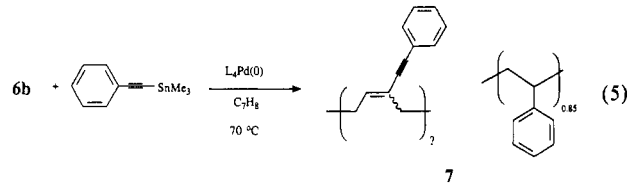


Figure 1. Thermogravimetric analysis of copolymer **6b** under an argon atmosphere. Heating rate was 10 °C/min.

most of which appears to be cross-coupling to afford copolymer **7** (eq 5). The ratio of the (*E*)- and (*Z*)-vinyl



(5)

isomers in **7** is very similar to the ratio observed in **6b**. Acyclic vinyl iodides possessing β-hydrogens often lead to poor yields in comparison with cyclic vinyl iodides or acyclic vinyl iodides which do not possess β-hydrogens.[10] The products arising from the side reaction are presently not known.

Vinyltributylstannanes are also known to undergo transmetalation with alkyllithium reagents to give the corresponding vinyllithium intermediates. The vinyllithium intermediates have been shown to be of great synthetic value.[11] The transmetalation step and subsequent reaction with an electrophile proceed with excellent stereospecificity.[11] In numerous attempts to carry out the transmetalation reaction with *n*-BuLi or CH_3Li, we obtain clean recovery of **4**. The vinyltributylstannane moiety in **4** appears to remain intact even when treated with MeLi/tetramethylethylene diamine at ambient temperature (eq 6).

$$4 \xrightarrow[Et_2O,\ 0\ °C]{CH_3Li} \xrightarrow{CH_3I} 4 \qquad (6)$$

Polymer Analyses. The thermal stability of **4** has been determined by using thermogravimetric analysis (TGA) under both argon and air. Under both atmospheres the copolymer shows similar thermal stability, giving a break point under air and argon of 326 and 328 °C, respectively. In both cases a residue is left behind which corresponds to the percent Sn in the copolymer. TGA analysis of copolymer **6b** is displayed in Figure 1. Differential scanning calorimeter (DSC) of **6b** shows an endotherm at 83 °C (likely T_m) and two exotherms at 290 (minor) and 300 °C (major). The two exotherms occur concomitantly with a total weight loss which is approximately equivalent to the percent I in the copolymer. Efforts to determine whether HI or I_2 is being eliminated from the polymer by using mass spectrometry have been unsuccessful. The minor exotherm at 290 °C might be attributed to decomposition of the 3,4-addition product that is not detected by infrared and ^1H NMR spectroscopies. One might expect a different exotherm for the 3,4-product due to the presence of a tertiary hydrogen. The major exotherm at 300 °C is interpreted to be the predominant 1,4-microstructure.

The present study demonstrates that palladium-catalyzed cross-coupling reactions represent a useful and potentially powerful method for polymer modification. Further development of this new method for polymer backbone modification is under way in our laboratory.

Experimental Section

General. All manipulations of compounds and solvents were carried out by using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying reagents. Spectroscopic measurements utilized the following instrumentation: ^1H NMR, Varian XL 300, NMR chemical shifts are reported in δ versus Me_4Si; infrared, Perkin-Elmer 1750 FT-IR spectrometer. The 2-chloro-1,3-butadiene was purchased from Alfa and distilled just prior to use for the synthesis of **1**. The tributylchlorostannane and AIBN were purchased from Aldrich Chemical Co. The AIBN was recrystallized from 95% ethanol and stored at −25 °C under nitrogen. Polymer analyses were carried out in the laboratory of Prof. J. K. Stille using a Du Pont 9900 thermal analysis data station with a 951 TGA module and a Du Pont DSC apparatus. Molecular weight analyses were measured in tetrahydrofuran solutions (0.1%, w/w) on a Waters Associates HPLC instrument against polystyrene calibration standards. Calculations of M_n and M_w were performed by using the standard GPC calculation package of Waters Associates. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Copolymerization of 2-(Tributylstannyl)-1,3-butadiene and Styrene. The AIBN (3 mol %) initiated copolymerization of **1**[12] (5.00 g, 14.6 mmol) and styrene (7.60 g, 73 mmol) was performed at 65 °C for 48 h in benzene (10 mL). The polymer was purified by multiple precipitations from methanol. Anal. Calcd for **4** (n = 0.15): C, 79.04; H, 8.30. Found: C, 78.88; H, 8.33. Distinctive ^1H NMR ($CDCl_3$) δ 5.20 (br s, vinyl CH).

Preparation of 5. To a DMF (5 mL) solution of **4** (0.50 g, 3.5 mmol) was added benzoyl chloride (0.12 g, 0.84 mmol) and vinyltributylstannane (0.11 mmol) to activate the catalyst. $(CH_3CN)_2PdCl_2$ (10 mol %) was added to the mixture at 25 °C and allowed to react for 16 h. The mixture was diluted with chloroform (50 mL) and the organic layer washed with water (3 × 50 mL). The organic layer was dried over K_2CO_3 and filtered through Celite, and the solvents were removed under reduced pressure. Polymer **5** was precipitated from cold pentane several times to remove the tributylchlorostannane and then dried under reduced pressure. Anal. Calcd for **5** (n = 0.15): C, 90.46; H, 7.42. Found: C, 87.80; H, 7.95. ^1H NMR ($CDCl_3$) δ 5.15 (br s, vinyl CH); IR (film) $\nu_{C=O}$ 1654 cm^{-1}.

Preparation of 6. Polymer **4** (1.50 g) was dissolved in $CHCl_3$ (10 mL) and titrated with a 0.10 M solution of I_2 until the purple color persisted, yielding polymer **6b** in 90% yield after precipitation from methanol. The polymer was dried at 65 °C under reduced pressure. Anal. Calcd for **6b** (n = 0.15): C, 77.02; H, 6.54; I, 16.50. Found: C, 77.15; H, 6.76; I, 15.87. ^1H NMR ($CDCl_3$) (peak areas 1:1) δ 5.90 (br s, vinyl CH), 4.95 (br s, vinyl CH). Polymer **6a** was prepared in a similar manner in 85% yield. Purification was done through repeated precipitations from methanol to afford **6a** as a white solid. ^1H NMR ($CDCl_3$) δ 5.46 (br s, vinyl CH) 5.08 (br s, vinyl CH). Anal. Calcd for **6a** (n = 0.15): Br, 11.06. Found: Br, 11.83.

Preparation of 7. A toluene (8 mL) solution of **6b** (0.50 g, 4.3 mmol) was treated with (phenylethynyl)trimethylstannane (0.21 g, 0.79 mmol) and $(Ph_3P)_2PdCl_2$ (2 mol %) and allowed to react at 70 °C for 12 h. The mixture was diluted with chloroform and washed with water and then brine. The organic layer was dried over K_2CO_3 and filtered, and the solvents were removed under reduced pressure. Final purification of the polymer (~28%) was achieved by repeated precipitations from methanol. Anal. Calcd for **7** (n = 0.15): C, 92.63; H, 7.44; I, 0.00. Found: C, 86.93; H, 7.36; I, 0.00. ^1H NMR ($CDCl_3$, 50 °C) δ 5.70 (br s, vinyl CH), 4.90 (br s, vinyl CH).

Acknowledgment. The authors express gratitude to the Office of the Vice President for Research at Utah State University for support of this work. M.E.W. also thanks Prof. J. K. Stille for the use of the polymer analysis equipment and Dr. Alex Parker for his kind assistance with the polymer characterizations.

Registry No. 4 (copolymer), 118476-48-5; $(MeCN)_2PdCl_2$, 14592-56-4; $(Ph_3P)_2PdCl_2$, 13965-03-2.

References and Notes

(1) Tobalsky, A. V.; Rogers, C. E. *J. Polym. Sci.* **1959**, *40*, 73. Sterns, R. S.; Forman, L. E. *J. Polym. Sci.* **1959**, *41*, 381. Worsford, D. J.; Bywater, S. *Can. J. Chem.* **1964**, *42*, 2884. Maynard, J. T.; Mochel, W. E. *J. Polym. Sci.* **1954**, *13*, 251.
(2) Aufdermarsh, C. A.; Pariser, R. *J. Polym. Sci.* **1964**, *A2*, 4727.
(3) Weber, W. P.; Ding, Y. *Macromolecules* **1988**, *21*, 530.
(4) Neumann, W. P. *The Organic Chemistry of Tin*; Wiley-Interscience: New York, 1970. Gielen, M. *Rev. Silicon, Germanium Tin Lead Compd.* **1981**, *5*, 6.
(5) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983; pp 79-97.
(6) For recent reviews in the area see: Stille, J. K. *Pure. Appl. Chem.* **1985**, *57*, 1771. Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.
(7) Craig, D.; Shipman, J. J.; Fowler, R. B. *J. Am. Chem. Soc.* **1961**, *83*, 2885. See also ref 2.
(8) Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630.
(9) Jung, M. E.; Light, L. A. *Tetrahedron Lett.* **1982**, *23*, 3851. Chen, Sow-Mei, L.; Schaub, R. E.; Grudzinskas, C. V. *J. Org. Chem.* **1978**, *43*, 3450.
(10) Stille, J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2138.
(11) Transmetalation reactions have been used extensively on vinylstannanes. For a recent application, see: Wulff, W. D.; Peterson, G. A.; Bauta, W. E.; Chan, K.; Faron, K. L.; Gilbertson, S. R.; Kaesler, R. W.; Yang, D. C.; Murray, C. K. *J. Org. Chem.* **1986**, *51*, 277, and references cited therein. For the initial report on the transmetalation reaction, see: Seyferth, D.; Weiner, M. A. *J. Am. Chem. Soc.* **1961**, *83*, 3583. Seyferth, D.; Vaughan, L. G. *J. Am. Chem. Soc.* **1964**, *86*, 883. Seyferth, D.; Weiner, M. A. *J. Am. Chem. Soc.* **1962**, *84*, 361.
(12) Wada, E.; Kanemasa, S.; Fujiwara, I.; Tsuge, O. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1942.

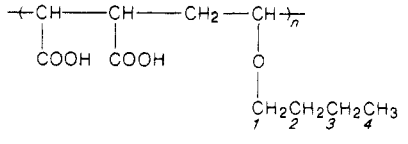
An NMR Study of the Solubilization of Aromatic Compounds in Aggregates of Poly(maleic acid-*co*-butyl vinyl ether) and Dodecyltrimethylammonium Bromide

ZHISHENG GAO, RODERICK E. WASYLISHEN, and JAN C. T. KWAK*

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3. *Received July 25, 1988; Revised Manuscript Received November 28, 1988*

Introduction

Poly(maleic acid-*co*-butyl vinyl ether) (PMA-BVE, I) is a water-soluble hydrophobic polymer,[1] which undergoes a transition from a compact conformation to an expanded



I

form with increasing ionization of the carboxylic acid groups.[2] The interactions between fully ionized PMA-BVE and cationic surfactants have recently been investigated by Binana-Limbele and Zana,[3] using solubilized pyrene as a fluorescence probe. The results of this study lead the authors to suggest that mixed micelles are formed with units of PMA-BVE and the cationic surfactants, which provide a nonpolar environment for the solubilized pyrene. Fluorescence probe studies of other polymer–surfactant aggregates in aqueous solution have also recently appeared.[4-8] These studies clearly indicate that polymer–surfactant complexes can solubilize some hydrophobic aromatic probe molecules into a nonpolar environment, similar to micellar solutions. It is of interest to further characterize the primary sites of solubilization in polymer–surfactant systems using other techniques. Ring current induced ^1H NMR shifts have been used to determine the location of aromatic solubilizates in micelles;[9-14] yet the technique has not been widely applied to polymer–surfactant systems.[15] If aromatic ring current induced shifts are observed for protons of the surfactant alkyl chain or for those of the polymer hydrophobic side chain, this is a clear indication of an average close proximity to the aromatic solubilizate, even though the absence of a ring current effect may only mean independent isotropic motion, rather than a large separation.[16] In this paper we report ring current shifts for surfactant and polymer side-chain proton resonances due to the solubilization of benzene, naphthalene, acridine, and pyrene in fully ionized PMA-BVE/dodecyltrimethylammonium bromide (DTAB) aggregates.

Experimental Section

PMA-BVE was prepared in our laboratory by the copolymerization of maleic anhydride and butyl vinyl ether in benzene using benzoyl peroxide as initiator.[17] Maleic anhydride and butyl vinyl ether (Aldrich) were purified by recrystallization from distilled benzene and by distillization at 93–94 °C, respectively. The butyl copolymer was dissolved in tetrahydrofuran (THF) and then successively precipitated into diethyl ether and vacuum dried. The resulting copolymer was added to a solution containing an equivalent amount of NaOH and kept at 80 °C for about 7 h; then excess HCl was added and the solution was dialyzed exhaustively against distilled water. The purified acid form of PMA-BVE was freeze dried and stored under vacuum. The copolymer was analyzed by means of IR, ^1H NMR, viscosity, and potentiometric titrations. The viscosity molecular weight of the copolymer anhydride in THF was determined to be 3.8×10^6.

The degree of neutralization, α', of PMA-BVE is defined as 1 for the acid form of the polymer neutralized with 2 equiv of base per monomer unit. The $\alpha' = 1$ sample used in the ^1H NMR measurements was obtained by titrating solid PMA-BVE (acid form) with 0.1120 *m* NaOD in D_2O. The pH of the final solution was about 8.5. At this pH, α' is very close to α, the degree of ionization of the polymer.

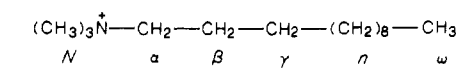
DTAB (Sigma) was purified by repeated recrystallization from acetone; the sample was the same as that used in an earlier surfactant-binding study.[18]

Polymer–surfactant solutions were prepared by slowly adding concentrated DTAB stock solution in D_2O to the PMA-BVE stock solution ($\alpha' = 1$) of known concentration. Although precipitation of a polymer–surfactant complex may occur due to local excesses of DTAB during addition, all solutions studied were completely clear after about 1 h of stirring. Aromatic solubilizates were added to the polymer–surfactant solution. All solutions were prepared by mass, and all concentrations are given as molalities (mol/kg of D_2O). Polymer concentrations are given on a monomer basis. D_2O was 99.8% pure (ICN).

^1H NMR spectra were recorded at 361.053 MHz (8.48 T), using a Nicolet 360NB spectrometer. The residue HOD ($\delta = 4.63$ ppm) was used as an internal reference for the proton spectra. All NMR measurements were carried out at 24 ± 1 °C.

Results and Discussion

The ^1H NMR spectrum of 0.020 *m* DTAB is shown in Figure 1a; the spectrum was assigned by using standard double resonance techniques.[15] The notation used to describe the various protons of surfactant segments is as follows:



The ^1H NMR spectrum of PMA-BVE(0.045 *m*)/DTAB(0.020 *m*) is shown in Figure 1b. Spectral assign-

0024-9297/89/2222-2544$01.50/0