

## Head-to-Head Polymers XXXV.† Head-to-Head Poly(2-vinylnaphthalene)

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**ABSTRACT:** Head-to-head poly(2-vinylnaphthalene) was prepared in five steps from 2-naphthylacetic acid. The methyl ester was brominated with *N*-bromosuccinimide and 2(2-naphthyl)2-bromoacetate treated with a copper/zinc couple, which gave dimethyl 2,3-di(2-naphthyl)succinate in moderate yield. This compound was reduced with lithium aluminum hydride to 2,3-di(2-naphthyl)butanediol-1,4 and the hydroxyl groups replaced by bromine. 2,3-Di(2-naphthyl)-1,4-dibromobutane was subjected to the Yamamoto coupling polycondensation; head-to-head poly(2-vinylnaphthalene) was obtained in relatively low yield and of modest molecular weight.

**KEY WORDS** Head-to-Head Polymers / Poly(2-vinylnaphthalene) / Yamamoto Polymerization / 2,3-Di(2-naphthyl)-1,4-dibromobutane / Head-to-Head Polystyrene / Photophysical Behavior /

The work on head-to-head (H-H) polymers in our laboratory has produced not only H-H polyacrylates and H-H poly(vinyl halides) but also H-H polyolefins.<sup>1-5</sup> Most carefully studied was H-H polystyrene<sup>6-11</sup> because the normal head-to-tail (H-T) polystyrene is a very important polymer and the comparison of various properties of H-H and H-T polymers was most desirable. The photophysical properties of H-T polystyrene showed that it forms excimers by intramolecular interactions of neighboring phenyl substituents. Studies of low molecular weight model compounds had shown that excimers formation was possible in 1,3-diphenylpropane but not in 1,2-diphenylethane nor in 1,4-diphenylbutane.

Our H-H polystyrene<sup>6,7</sup> was the ideal example of this hypothesis. It was indeed found<sup>12,13</sup> that no excimers were identifiable in H-H polystyrene.

This conclusion and our general interest in the study of the spectral and thermal behavior of H-H polymers made the synthesis of H-H poly(vinylnaphthalenes) desirable. We have already reported the synthesis of H-H poly(1-vinylnaphthalene) (P1VN).<sup>14,15</sup>

It was now our objective to synthesize H-H poly(2-vinylnaphthalene) (P2VN), to study its spectral and thermal behavior, and to compare its properties with H-T P2VN and other H-H polymers (Equation).

### EXPERIMENTAL

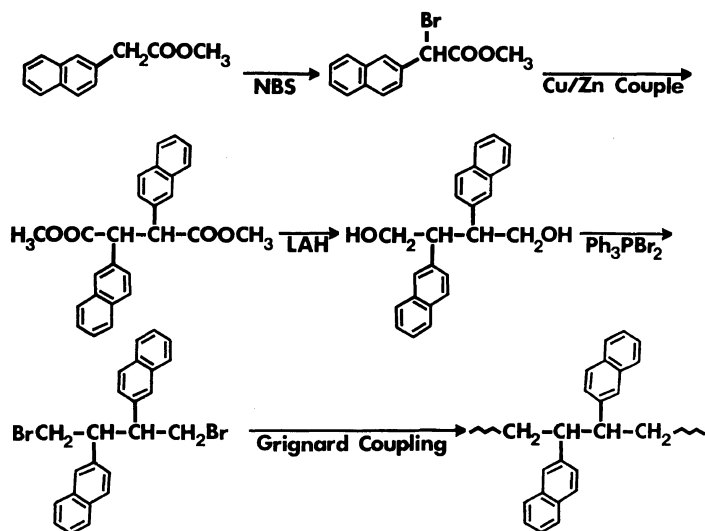
#### *Materials*

Methyl 1-naphthylacetate was prepared from 1-naphthylacetic acid and methanol with sulfuric acid as the catalyst; bp 125—126 °C/2.5 mmHg (lit 16): 160—170°C/15—20 mmHg.

Zinc powder was activated with copper(II)

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chloride before use. Copper(I) tris(triphenylphosphine)bromide was prepared according to the literature,<sup>17</sup> mp 176—178°C (lit, mp 167 °C). 2,2-Azobisisobutyronitrile (AIBN) was purified as previously described.<sup>6</sup> Tetrahydrofuran (THF) was purified by heating to reflux with excess lithium aluminum hydride (LAH); it was then distilled under nitrogen. For the Grignard coupling polymerization, THF was further purified by distilling it from the sodium benzophenone complex. Magnesium powder was used as received from Aldrich Chemical Co. (50 mesh, purity 99+%). Carbon tetrachloride and acetonitrile were treated with molecular sieves 3A prior to their use.

Other chemicals and solvents were used as supplied.

#### Measurements

Melting points were measured in a capillary tube on a MELT-TEMP melting point apparatus at a heating rate of 2° min<sup>-1</sup> and are uncorrected.

Infrared spectra were recorded on a Perkin-Elmer Model 727 spectrometer and <sup>1</sup>H spectra on a JEOL FX 90 Q NMR spectrometer. Ultraviolet spectra were measured in tetrahy-

drofuran solution (~10<sup>-5</sup> molar) on a Cary 2300 spectrophotometer.

The thermal behavior of the polymers was studied by differential scanning calorimetry at a heating rate of 10°C min<sup>-1</sup> under nitrogen on a Perkin-Elmer-7 scanning calorimeter.

Elemental analyses were performed by the Microlytics Co., South Deerfield, MA 01373.

#### Procedures

1. *Methyl 2-naphthylacetate*: Methyl 2-naphthylacetate was prepared from 2-naphthylacetic acid and methanol in the presence of sulfuric acid as the catalyst; bp 126—128°C/0.3 mmHg; mp 25—26°C.

2. *Methyl 2-Bromo-2-(2-naphthyl)acetate (MB2NA)*: The mixture of methyl 2-naphthylacetate (30 g, 150 mmol) and *N*-bromosuccinimide (32 g, 178 mmol) in carbon tetrachloride (200 ml) was heated to gentle reflux with stirring. To this mixture, 5 drops of bromine and AIBN (500 mg) were added, the reaction mixture was heated to reflux for 4 h and then cooled in an ice bath. Succinimide, which had separated, was removed by filtration, the filtrate washed with carbon tetrachloride, and the combined solutions concentrated under reduced pressure. The oily

residue was recrystallized from benzene/*n*-hexane (1:15). Yield: 38 g (92%); mp 39—41°C.

*Elemental Analysis.* Found: C, 55.21%; H, 3.97%. Calcd for C<sub>13</sub>H<sub>11</sub>BrO<sub>2</sub>: C, 55.94%, H, 3.97%. <sup>1</sup>H NMR (CDCl<sub>3</sub> solution), δ in ppm 3.78 (s, 3H, CH<sub>3</sub>), 5.54 (s, 1H, —CH—), and 7.4—7.9 (m, 7H, ArH).

*Dimethyl 2,3-Di(2-naphthyl)succinate (DM2NS):* To a suspension of anhydrous cupric chloride (35.6 g, 265 mmol) and anhydrous THF (600 ml) under a nitrogen atmosphere was added activated zinc powder (17.3 g, 265 mmol) and mercury(II) bromide (0.2 g); this mixture was stirred at room temperature for 15 min and then cooled in an ice bath. Methyl 2-bromo-2-(2-naphthyl)acetate (37 g, 132 mmol) in anhydrous THF (50 ml) was added dropwise to this mixture over a period of 20 min; the reaction mixture was stirred at room temperature for 30 min and then heated to reflux. After 2 h, the reaction mixture was cooled to room temperature, the inorganic salts which had precipitated were separated by filtration, and the solid washed with THF. The filtrate was concentrated under reduced pressure, the residue dissolved in warm chloroform (200 ml), the solution washed with 1% aqueous hydrochloric acid and water, dried over anhydrous sodium sulfate, and then concentrated under reduced pressure.

The semisolid which was left was stirred in hot methanol (200 ml) and the solution was cooled in an ice bath. A solid precipitated which was filtered, washed thoroughly with diethyl ether and dried under reduced pressure. Yield: 6.75 g (26%); mp 216—222°C.

*Elemental Analysis:* Found: C, 78.13%; H, 5.57%. Calcd for C<sub>26</sub>H<sub>22</sub>O<sub>4</sub>: C, 78.37%; H, 5.57%.

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>), δ in ppm: 3.32 (s, 4.2H, *meso*-CH<sub>3</sub>), 3.63 (s, 1.3H, *rac*-CH<sub>3</sub>), 3.93 (s, 0.5H, *rac*-CH), 4.72 (s, 1.4H, *meso*-CH), and 7.3—8.0 (m, 14H, ArH).

3. 2,3-Di(2-naphthyl)butanediol-1,4

(*D2NBD*): The solution of dimethyl 2,3-di(2-naphthyl)succinate (6.0 g, 15 mmol) in anhydrous THF (200 ml) was added dropwise to the suspension of LAH (2.4 g, 60 mmol) in THF (50 ml) which had been cooled in an ice bath. After the addition (15 min), the reaction mixture was stirred at room temperature for 30 min and then heated to reflux for 1 h. The mixture was cooled in an ice bath and aqueous 15% sodium hydroxide (2 ml) and water (2 ml) were added to the vigorously stirred mixture. The organic salts, which had precipitated, were separated by filtration and thoroughly washed with hot THF.

The filtrate was concentrated under reduced pressure; the residual oil was dissolved in diethyl ether (30 ml), and the solution was cooled to -15°C.

The product that had precipitated was isolated by filtration and washed with cold diethyl ether/*n*-hexane (1:3). Yield: 3.6 g (69%); mp 155—161°C.

*Elemental Analysis.* Found: C, 84.32%; H, 6.67%. Calcd for C<sub>24</sub>H<sub>22</sub>O<sub>2</sub>: C, 84.18%; H, 6.48%.

IR (KBr pellet): 3200—3560 (OH), 1050 (C—O)cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>), δ in ppm: 3.3—3.4 (OH), 2.9—3.8 (CH<sub>2</sub>), 4.3—4.7 (CH), 7.4—7.9 (Naph).

4. 2,3-Di(2-naphthyl)1,4-dibromobutane (*D2NDB*): To a solution of triphenyl phosphine (6.81 g, 25 mmol) in dry acetonitrile (35 ml) in a dry nitrogen atmosphere, bromine (1.22 ml, 24 mmol) was added dropwise with stirring, and the reaction mixture was continued to be stirred for 15 min at room temperature. The solution was cooled in an ice bath and 2,3-di(2-naphthyl)-butanediol-1,4 (2.90 g, 8.5 mmol) in acetonitrile (50 ml) was added dropwise; the mixture was stirred at room temperature for 30 min and then gradually heated to reflux. After 3.5 h, the reaction mixture was cooled in an ice bath, the solid which had precipitated was separated by filtration and washed with acetonitrile and methanol. Yield: 3.34 g (84%); mp 233—235

°C.

*Elemental Analysis.* Found: C, 61.70%; H, 4.22%. Calcd for  $C_{24}H_{20}Br_2$ : C, 61.56%; H, 4.31%.

IR (KBr pellet): 1250 ( $-CH_2-Br$ )  $cm^{-1}$ .  $^1H$  NMR (DMSO- $d_6$ ),  $\delta$  in ppm: 3.51 (4H,  $CH_2$ ), 3.61 (2H, CH), 7.52, 7.82, and 8.14 (14H, Naph).

5. *H-H Poly(2-vinylnaphthalene) (P2VN)*: In a 50 ml three-neck flask equipped with a reflux condenser and a nitrogen inlet and exit was placed the magnesium powder; the reaction flask was flamed out and cooled under a stream of nitrogen.

A 5 ml solution of 2,3-di(2-naphthyl)1,4-dibromobutane (900 mg, 1.9 mmol) and copper(I) tris(triphenylphosphine)bromide (20 mg) in THF (25 ml) and an iodine crystal ( $\sim 10$  mg) were added to the flask, and the reaction mixture was heated to reflux. After the iodine color had started to fade, the remaining THF solution of the dibromide was added dropwise from a syringe to the refluxing mixture, which was continued to be heated to gentle reflux for 3 h; the gray solution was poured into 150 ml of methanol containing 5 drops of concentrated hydrochloric acid, and the mixture was allowed to stand overnight. A suspension had formed which was filtered, the solid washed with methanol and purified by precipitating the toluene solution of the polymer into methanol. Yield: 71 mg (12%);  $[\eta] = 0.085$  dl  $g^{-1}$  (0.5% toluene solution at 25°C);  $T_g$  (DSC) = 146°C.

*Elemental Analysis.* Found: C, 92.60%, H, 6.57%. Calcd for  $C_{24}H_{20}$ : C, 93.46; H, 6.54%.

IR (KBr pellet), 2880 ( $CH_2$ ), 1600, 1510, 860, 820, and 745 (Naph)  $cm^{-1}$ .

## RESULTS AND DISCUSSION

H-H P2VN was prepared in a sequence of five steps starting from methyl 2-naphthylacetate. 2-Naphthylacetic acid was esterified with methanol and sulfuric acid in 90%

yield. Methyl 2-naphthylacetate was brominated with *N*-bromosuccinimide in the usual way by radical bromination in carbon tetrachloride as the solvent. The radical bromination was slow, even when AIBN was added as the radical initiator for the bromination; as a consequence, bromine was used as the initiator for the *N*-bromosuccinimide bromination, which then proceeded smoothly. Ionic bromination using the Hell-Volhard-Zelinsky bromination method gave only ring brominated products.

There are some small differences in the spectral behavior of the methyl 2-bromo-2(2-naphthyl)acetate, and methyl 2-bromo-2(1-naphthyl)acetate. The  $^1H$  NMR spectrum showed that the chemical shift value of the proton which is substituted on the carbon atom which also has the naphthyl ring and the bromine substituent is shifted by about 0.6 ppm to higher field. This difference is large as compared to the difference in the chemical shift value of the two isomers in the corresponding naphthylacetic acids. (1-Naphthylacetic acid has a chemical shift value for the methylene protons of 3.95 ppm, and 2-naphthylacetic acid of 3.72 ppm.) This difference can possibly be caused by the steric hindrance of the carbon atom in the 8-position of the 1-naphthyl compound which may be caused by the large ring substituted on the benzylic carbon atom.

Dimethyl 2,3-di(2-naphthyl)succinate was prepared by coupling reaction of methyl 2-bromo-2(2-naphthyl)acetate with the copper/zinc couple in about 30–40% yield. In addition, some methyl 2-naphthylacetate was also obtained by reductive debromination of methyl 2-bromo-2(2-naphthyl)acetate. Dimethyl 2,3-di(2-naphthyl)succinate was reduced with LAH in THF to 2,3-di(2-naphthyl)-butanediol-1,4. The reaction conditions for this reaction were similar to those which produced 2,3-di(1-naphthyl)butanediol-1,4 from dimethyl 2,3-di(1-naphthyl) succinate. 2,3-Di(2-naphthyl)butanediol-1,4 is a mixture

of the *meso*- and racemic isomer; the mixture could be used for the next step of our synthesis the bromination of the glycol by replacement of the two hydroxyl groups in the 1- and 4-position of the 2,3-disubstituted butanediol-1,4 with bromine.

The replacement of the hydroxyl groups of 2,3-di(2-naphthyl)butanediol-1,4 was accomplished with triphenylphosphine dibromide in acetonitrile. The mixture of the two disubstituted diols should give the mixture of the two isomers of 2,3-di(2-naphthyl)1,4-dibromobutane, but in actual fact, only pure *meso* 2,3-di(2-naphthyl)1,4-dibromobutane was isolated from the reaction mixture. It might be interesting to note that the 2-naphthyl derivatives of the 2,3-di(2-naphthyl)1,4-dibromobutanes and the 2,3-di(2-naphthyl)butanediols-1,4 show a lower melting point than do those of the corresponding 1-naphthyl derivatives. It could well be that the rotation of the 1-naphthyl derivatives along the carbon-(1-naphthyl) bond is more restricted by the hydrogen atom in the 8-position of the naphthalene ring, causing a more regular structure and higher melting points.

2,3-Di(2-naphthyl)1,4-dibromobutane was subjected to Grignard polycondensation using magnesium and copper(I) tris(triphenylphosphine)bromide in THF. The intermediate compound of this reaction is most likely a copper compound formed from the

Grignard reagent. In spite of various combinations of reaction conditions, the yield of polymer was always relatively low; in addition, the molecular weight of the H-H P2VN was also relatively low (see, however, ref 18).

H-T P2VN was prepared by radical polymerizations of 2-vinylnaphthalene with azobisisobutyronitrile in toluene solution in an evacuated tube with freeze-thaw technique, similar to careful radical polymerizations traditionally carried out in our laboratory. The IR spectrum of H-T P2VN is indistinguishable from that of H-H P2VN (KBr pellet, Figure 1). The  $^{13}\text{C}$  NMR spectrum showed small but very distinct differences between the H-T and H-H polymer (Figure 2). The ultraviolet spectrum of the H-T P2VN is also very similar to that of the H-H P2VN, although small but very significant differences between the H-H and H-T polymers can be seen in the 250 nm and the longer wavelength region (Figure 3), which could be caused by conjugation of naphthalene rings with vinyl end groups of low molecular weight H-H P2VN fraction. In our spectral representation of H-H, H-T P2VN and D2NDB, we show the line shapes of the spectra for comparison without specifying the extinction coefficient of the ultraviolet spectra of the individual compounds because the line shapes and extinction coefficients of all these com-

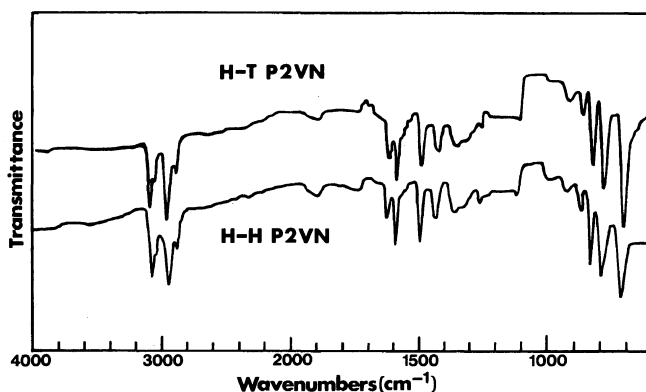


Figure 1. IR spectra (KBr) of H-T poly(2-vinylnaphthalene) and H-H poly(2-vinylnaphthalene).

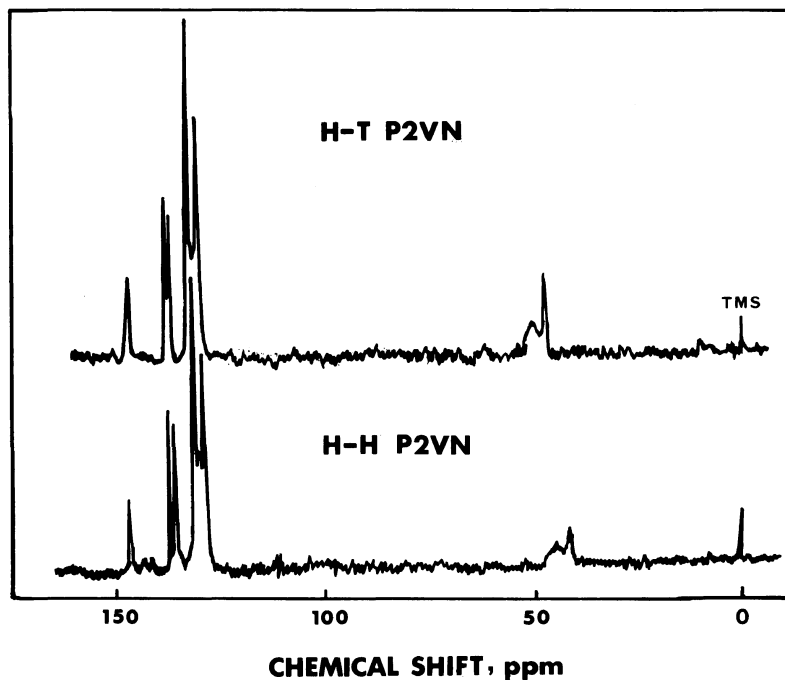


Figure 2.  $^{13}\text{C}$  NMR spectra ( $\text{CDCl}_3$  solution) of H-T poly(2-vinylnaphthalene) and H-H poly(2-vinylnaphthalene).

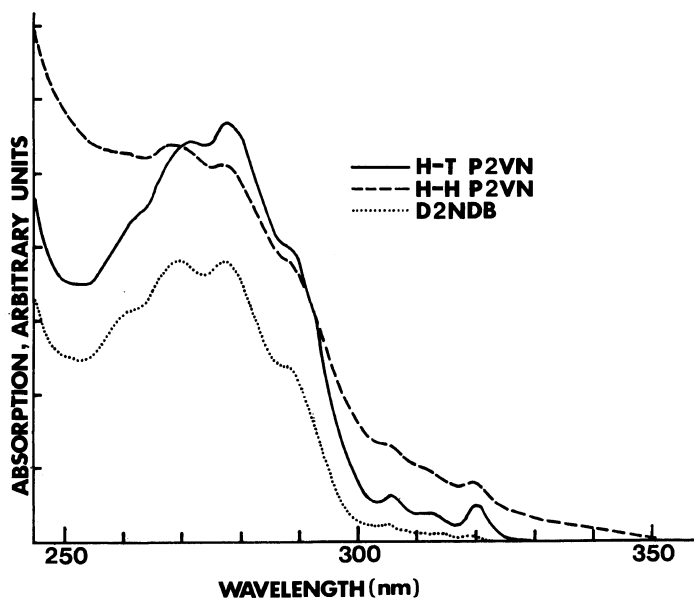


Figure 3. UV spectra: —, H-T poly(2-vinylnaphthalene); - - -, H-H poly(2-vinylnaphthalene); ····, 2,3-di(2-naphthyl)-1,4-dibromobutane.

pounds are similar.

One of the side reactions that could possibly be detrimental to the achievement of high yields and high molecular weight of H-H P2VN is the dehydrobromination reaction which occurs to some extent during the formation of the Grignard reagent by the loss of the  $\alpha$ -hydrogen atoms and the formation of vinyl groups. In addition to the normal Grignard reaction product and compounds that contain vinyl end groups, oligomers and polymers that have the  $\text{CH}_2\text{Br}$  end groups are obtained.

Possible side reactions in these polycondensations are the formation of vinyl end groups or, in an extreme case, the formation of 2,3-di(2-naphthyl)butadiene-1,3. Low molecular weight oligomers with vinyl ends are also expected side products which limit the formation of high molecular weight polymers. At the scale on which we have carried out the polycondensation reactions, no pure compounds were isolated, although it was quite likely that some of these oligomers could be isolated if the Yamamoto polymerizations were carried out on a larger scale.

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