# Head-to-head polymers: 34. Head-to-head poly(1-vinylnaphthalene)*

**Masato Nanasawa, Liping Hu and Otto Vogl†**
*Polytechnic Institute of New York, Brooklyn, NY 11201, USA*
*(Received 24 March 1986; revised 27 June 1986)*

Head-to-head poly(1-vinylnaphthalene) was synthesized by a sequence of five reactions and the polymer was characterized by its infra-red and nuclear magnetic resonance spectra. Methyl 1-naphthylacetate was brominated to methyl 2-bromo-2(1-naphthyl)acetate, which was coupled with a copper–zinc couple to dimethyl 2,3-di(1-naphthyl)succinate, a mixture of stereoisomers, which was separated into the meso and racemic compounds. Lithium aluminium hydride reduction of dimethyl 2,3-di(1-naphthyl)succinate gave 2,3-di(1-naphthyl)butanediol-1,4; the two hydroxyl groups were replaced with bromine to 2,3-di(1-naphthyl)-1,4-dibromobutane. Polymerization by Grignard coupling reaction with copper/salt catalysts gave head-to-head poly(1-vinylnaphthalene) in low yield and of relatively low molecular weight.

**(Keywords: head-to-head polymers; poly(1-vinylnaphthalene); Yamamoto polymerization; methyl 1-naphthylacetate; 2,3-di(1-naphthyl)-1,4-dibromobutane)**

## INTRODUCTION

In our work on head-to-head (H-H) vinyl polymers, we have synthesized a number of these polymers, studied their chemical, physical and thermal properties, and compared them with those of the corresponding head-to-tail (H-T) vinyl polymers[1-3].

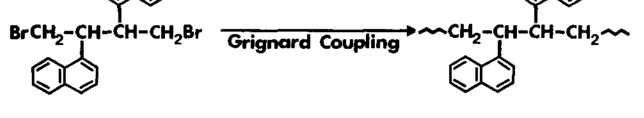
In this article we wish to report the first synthesis of H-H poly(1-vinylnaphthalene) (P1VN). H-T poly(vinylnaphthalenes) are some of the oldest polymers[4] known and a number of their chemical and physical properties have been reported. Recently, poly(vinylnaphthalenes) have become of interest because of their potential in photoconductivity[5,6] and as electron-beam-resist[7] polymers.

H-H polystyrene has been prepared[8,9] in the past and its photochemical behaviour[10] was studied. H-T polystyrene readily forms excimers[11,12] but there is no evidence of intramolecular excimer formation or energy migration in H-H polystyrene. H-H P1VN, however, could be expected to have some intramolecular interaction. When its 1-naphthyl group was placed in the polyethylene chain in 1,2 and 1,4 positions (H-H placement), because of the bulky naphthalene ring and the possibility of an overlapping ring current, some excimer formation could be possible.

The synthesis of H-H P1VN was therefore of considerable interest; the physical and thermal properties and the photochemical behaviour of H-H P1VN were the focus of our attention.

For the preparation of H-H P1VN, two principal methods of synthesis were considered: (a) polycondensation of 2,3-di(1-naphtyl)-1,4-dihalobutane by our modification of the Yamamoto coupling technique[13] and (b) polymerization of 2,3-di(1-naphthyl)butadiene-1,3 followed by hydrogenation of the 1,4-poly(2,3-substituted)butadiene-1,3. (A polymerization similar to this one was successfully carried out as the first step in the preparation of H-H polystyrene from 2,3-diphenylbutadiene-1,3[8,9] and of H-H polypropylene from 2,3-dimethylbutadiene-1,3[14,15].) Method (b) as a route to H-H P1VN did not give the desired polymer; the polymerization of 2,3-di(1-naphthyl)butadiene-1,3 could be successfully carried out but the selective hydrogenation of the main chain double bond could not be achieved; hydrogenation of the naphthyl rings occurred always concurrently with the reduction of the main chain double bond.

We are reporting here the successful synthesis of H-H P1VN* by the coupling polymerization of 2,3-di(1-naphthyl)-1,4-dibromobutane:



## EXPERIMENTAL

### *Materials*

Methyl 1-naphthylacetate was prepared from 1-naphthylacetic acid and methanol with sulphuric acid as

---

* Part 33: Kawaguchi, H., Loeffler, P. and Vogl, O. *Polymer* 1985, **26**, 1267

† To whom all correspondence should be addressed

* H-H poly(1-vinylnaphthalene): These structures as written do not imply any specific stereochemistry of the polymer structure

0032-3861/87/030514-05$03.00

the catalyst: b.p., 144–145°C at 2.5 mmHg[16], 160–170°C at 15–20 mmHg.

Zinc powder was activated with copper(II) chloride before use[14]. Copper (I) tris(triphenylphosphine)bromide was prepared according to the literature[13]: m.p., 176–178°C (literature value, 167°C). 2,2-Azobisisobutyronitrile (AIBN) was purified as previously described[8]. Tetrahydrofuran (THF) was purified by heating it to reflux with excess lithium aluminium 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 above 99%). Carbon tetrachloride and acetonitrile were treated with molecular sieves 3A prior to their use.

H-T P1VN was prepared by radical polymerization of 1-vinylnaphthalene in vacuum with AIBN; from viscosity measurements and nitrogen endgroup analysis (from the isobutyronitrile radical obtained from AIBN initiation, assuming one endgroup per molecule) the $M_n$ of H-T P1VN was about 5000.

Other chemicals and solvents were used as supplied.

### *Measurements*

Melting points were determined in a capillary tube on a Melt-Temp melting point apparatus at a heating rate of 2°C min$^{-1}$ and are uncorrected.

Infra-red (i.r.) spectra were recorded on a Perkin–Elmer model 727 spectrometer and the $^1$H nuclear magnetic resonance (n.m.r.) spectra on a Jeol FX 90 Q n.m.r. spectrometer.

The thermal behaviour of the polymers was studied by differential scanning calorimetry at a heating rate of 10°C min$^{-1}$ under nitrogen on a Perkin–Elmer 7 scanning calorimeter.

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

### *Synthesis procedures*

*Methyl 2-bromo-2(1-naphthyl)acetate* (*MB1NA*). A mixture of methyl 1-naphthylacetate (13.5 g, 0.69 mol) and *N*-bromosuccinimide (144 g, 0.81 mol) in carbon tetrachloride (900 ml) was heated to reflux with stirring while AIBN (400 mg) was added in small portions. The reaction mixture was continued to be heated to reflux for 3 h and then cooled in an ice bath. Succinimide was removed by filtration and washed with carbon tetrachloride. The filtrate and washings were concentrated under reduced pressure; an oily product remained which was fractionally distilled. MB1NA: yield, 17.1 g (89%); b.p. 155–160°C at 0.5 mmHg.

Elemental analysis: found, C 55.68%, H 3.87%; calculated for $C_{13}H_{11}BrO_2$, C 55.94%, H 3.97%.

I.r. (neat): 1755 cm$^{-1}$ (C=O), 1250 cm$^{-1}$ (-CHBr). $^1$H n.m.r. ($CDCl_3$): $\delta$ (ppm), 3.59 (s, 3H, $CH_3$), 6.17 (s, 1H, –CH–), 7.16–8.2 (m, 7H, ArH).

*Meso dimethyl 2,3-di(1-naphthyl)succinate)* (*mDM1NS*). Anhydrous copper(II) chloride[14] (77.4 g, 0.57 mol) and anhydrous THF (1300 ml) were stirred with a mechanical stirrer under a nitrogen atmosphere; activated zinc powder (37.5 g, 0.57 mol) and mercury(II) bromide (0.13 g) were added to the suspension. MB1NA (80 g, 0.29 mol) in anhydrous THF (100 ml) was added dropwise; the reaction mixture was stirred for 2 h at room temperature and then heated to reflux for 2 h. After allowing the reaction mixture to stand overnight, the white solid, which had precipitated, was removed by filtration and washed with THF. The filtrate was concentrated under reduced pressure and the oily residue was poured into a vigorously stirred 2% aqueous hydrochloric acid solution (1000 ml). The yellow oil was dissolved in chloroform (400 ml), the solution was washed with water, 5% aqueous sodium bicarbonate solution, and again with water, dried over anhydrous sodium sulphate, and concentrated under reduced pressure. The residue was dissolved in methanol (800 ml) and the solution placed in a refrigerator. A compound which was later identified as mDM1NS precipitated and was isolated by filtration. Recrystallization from THF gave pure mDM1NS in a yield of 12.3 g (21.5%), m.p. 251–253°C.

Elemental analysis: found, C 78.45%, H 5.77%; calculated for $C_{28}H_{22}O_4$, C 78.37%, H 5.57%.

I.r. (KBr pellet): 1730 cm$^{-1}$ (C=O), 1300 cm$^{-1}$ (C–O). $^1$H n.m.r. (DMSO-$d_6$): $\delta$ (ppm), 3.14 (s, 6H, –$CH_3$), 5.65 (s, 2H, CH), 7.5–7.7 (m, 3,6,7-ArH), 7.9–8.0 (m, 6H, 2,4,5-ArH), 8.55 (q, 2H, 8-ArH).

*Racemic dimethyl 2,3-di(1-naphthyl)succinate* (*rDM1NS*). The methanol filtrate, after mDM1NS was removed by filtration, was concentrated under reduced pressure; the residue was distilled at 0.1 mmHg (160°C oil bath) to remove methyl 1-naphthylacetate which was formed as a by-product of the zinc–copper coupling reaction by reductive debromination. The viscous residue which remained was stirred in diethyl ether (150 ml); rDM1NS gradually solidified and was recrystallized from acetone. Yield, 8.2 g (15%), m.p. 172–176°C.

Elemental analysis: found, C 78.17%, H 5.40%; calculated for $C_{26}H_{22}O_4$, C 78.37%, H 5.57%.

I.r. spectrum: similar to that of mDM1NS. $^1$H n.m.r. spectrum (DMSO-$d_6$): $\delta$ (ppm), 3.60 (s, 6H, $CH_3$), 5.51 (s, 2H, CH), 7.2–7.8 (m, 12H, ArH), 8.1 (d, 2H, 8-ArH).

*Meso and racemic 2,3-di(1-naphthyl)butane-1,4-diol* (*D1NBD*). These were synthesized by reduction of DM1NS with LAH in anhydrous THF; the work-up was done as is customary for LAH reductions[14,20].

*mD1NBD:* yield, 83%; m.p. 202–204°C.

Elemental analysis: found, C 83.94%, H 6.53%; calculated for $C_{24}H_{22}O_2$, C 84.18%, H 6.48%.

I.r. (KBr pellet): 3550 cm$^{-1}$, 3450 cm$^{-1}$ (OH), 1065 cm$^{-1}$ (C–O). $^1$H n.m.r. (DMSO-$d_6$): $\delta$ (ppm), 3.61 (broad s, 4H, $CH_2$), 4.24 (s, 2H, OH), 4.34 (t, 2H, CH), 7.4–7.6 (m, 6H, 3,6,7-ArH), 7.7–7.9 (m, 6H, 2,4,5-ArH), 8.25 (d, 2H, 8-ArH).

*rD1NBD:* yield, 82%; m.p. 186–188°C.

Elemental analysis: found, C 84.05%, H 6.50%; calculated for $C_{24}H_{22}O_2$, C 84.18%, H 6.48%.

I.r. (KBr pellet): 3200 cm$^{-1}$ (OH), 1062 cm$^{-1}$ (C–O). $^1$H n.m.r. (DMSO-$d_6$): $\delta$ (ppm), 3.92 (broad s, 4H, $CH_2$), 4.52 (s, 2H, CH), 4.91 (t, 2H, CH), 7.0–7.2 (m, 4H, 6,7-ArH), 7.5–7.6 (m, 6H, 2,3,5-ArH), 7.75 (q, 2H, 4-ArH), 8.39 (d, 2H, 8-ArH).

*2,3-Di(1-naphthyl)-1,4-dibromobutane* (*D1NDB*). To the solution of triphenylphosphine (19.6 g, 74 mmol) in dried acetonitrile (100 ml), bromine (3.6 ml, 69 mmol) was added dropwise with stirring under nitrogen atmosphere, and the stirring of the reaction mixture was continued for 15 min at room temperature. mD1NBD

(8.5 g, 25 mmol) in dried acetonitrile (200 ml) was added dropwise to the cooled triphenylphosphine dibromide solution; the reaction mixture was stirred at room temperature for 1 h and then heated to reflux for 4 h. After standing in a refrigerator overnight, the dibromide (mD1NDB) had precipitated; it was filtered, washed with acetonitrile, and then recrystallized from benzene.

*mD1NDB:* yield, 10.9 g (94%); m.p. 248–250°C.

Elemental analysis: found, C 61.34%, H 4.31%; calculated for $C_{24}H_{20}Br_2$, C 61.56%, H 4.31%.

I.r. (KBr): 1255 cm$^{-1}$ (C–Br). $^1$H n.m.r. (DMSO-$d_6$): $\delta$ (ppm), 3.5–3.9 (m, 4H, $CH_2$), 4.59 (t, 2H, CH), 7.5–7.6 (m, 6H, 3,6,7-ArH), 7.8–8.0 (m, 6H, 2,4,5-ArH), 8.2–8.3 (m, 2H, 8-ArH).

*rD1NDB:* yield, 89%; m.p. 175–176°C (recrystallized from MeOH).

Elemental analysis: found, C 61.47%, H 4.42%; calculated for $C_{24}H_{20}Br_2$, C 61.56%, H 4.31%.

$^1$H n.m.r. (DMSO-$d_6$): $\delta$ (ppm), 4.25 (q, 4H, $CH_2$), 4.80 (s, 2H, CH), 7.10 (q, 2H, ArH), 7.3–7.8 (m, 10H, ArH), 8.30 (d, 2H, 8-ArH).

*Polymerization of D1NDB by modified Yamamoto coupling*. A 100 ml three-necked flask equipped with a calcium chloride tube and a nitrogen inlet and exit was flamed out and cooled under a flow of dry nitrogen. Magnesium powder (54 mg, 2.2 mmol) was charged and the reaction flask was dried once more. A solution of D1NDB (945 mg, 2.0 mmol) in warm THF (15 ml) was made. Some of this solution (3 ml) and a small amount of iodine crystals (~5 mg) were added to the flask to start the reaction. The mixture was heated until the reaction became clearly noticeable. The heating was then stopped and the remaining dibromide was added dropwise at room temperature; the reaction mixture was stirred at room temperature overnight (all of the magnesium metal was consumed in about 2 h) to assure completion of the reaction.

After cooling in an ice-salt bath (−5°C), copper(I) tris(triphenylphosphine)bromide (5.0 mg) was added; the mixture was stirred for 2 h and then at room temperature for 24 h. The solution was poured into methanol (100 ml) containing two drops of concentrated hydrogen chloride solution which caused the polymer to precipitate; the suspension was filtered, the solid washed with methanol and purified by precipitating the toluene solution of the polymer into methanol. Yield, 80 mg (13%); $[\eta]=0.075$ dl g$^{-1}$ (toluene at 25°C).

Elemental analysis: found, C 92.11%, H 5.56%, Br 1.7%; calculated for $C_{24}H_{20}$, C 93.46%, H 6.54%.

I.r. (KBr): 2925 cm$^{-1}$, 2870 cm$^{-1}$ (–$CH_2$–) (*Figure 1*). $^1$H n.m.r. ($C_6D_6$): $\delta$ (ppm), 1.56 (6H, $C\underline{H}_2$, 2.99 (4H, $C\underline{H}$), 7.40 (14H, $Ar\underline{H}$). $^{13}$C n.m.r. ($C_6D_6$): $\delta$ (ppm), 33.9–34.5 ($\underline{C}H_2$), 44.4–45.8 ($\underline{C}H$), 142.2 (8-Ar$\underline{C}$) (*Figure 2*).

U.v spectrum (THF): $\lambda_{max}=287$ nm ($\varepsilon=1.07\times10^4$), 277 (sh) nm ($\varepsilon=9.12\times10^3$), 297 (sh) nm ($\varepsilon=8.32\times10^3$ l cm$^{-1}$ mol$^{-1}$) (*Figure 3*).

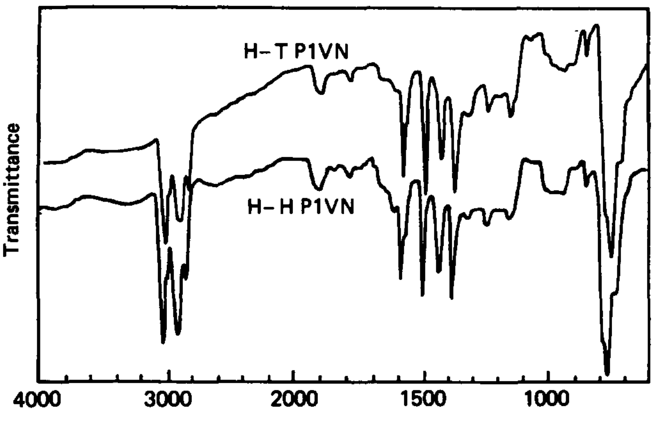


**Figure 1** I.r. spectra (KBr) of H-T poly(1-vinylnaphthalene) and H-H poly(1-vinylnaphthalene)

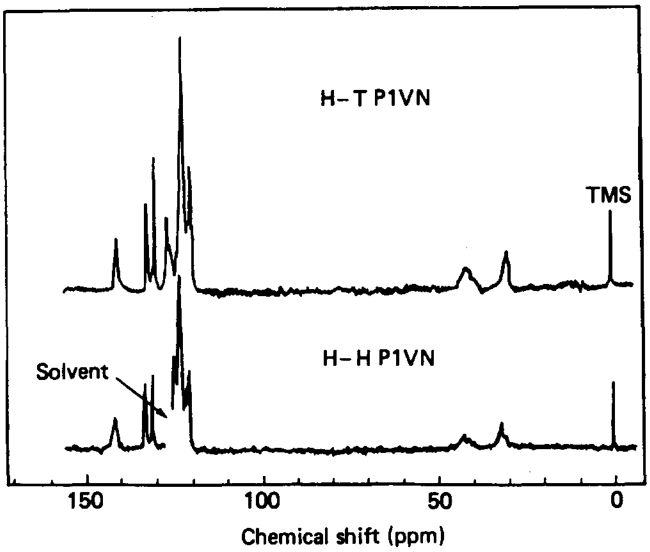


**Figure 2** $^{13}$C n.m.r. spectra ($CDCl_3$ solutions) of H-T poly(1-vinylnaphthalene) and H-H poly(1-vinylnaphthalene)

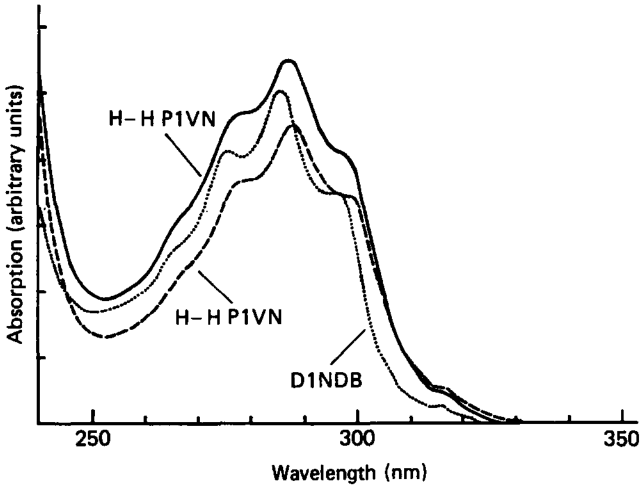


**Figure 3** U.v. spectra of H-T poly(1-vinylnaphthalene) (– – –), H-H poly(1-vinylnaphthalene) (———) and 2,3-di(1-naphthyl-1,4-dibromobutane (·····)

## RESULTS AND DISCUSSION

The starting material for the synthesis of H-H D1VN by Grignard coupling polymerization was methyl 1-naphthylacetate, which was brominated with *N*-bromosuccinimide. MB1NA was obtained in high yields (90%) by radical bromination at the methylene group in the benzylic position. The $^1$H n.m.r. spectrum of MB1NA showed the methyl and methine protons at 3.59 and 6.17 ppm. MB1NA was used for the coupling reaction with a zinc–copper couple to DM1NS. This type of coupling reaction of α-halo esters with a zinc–copper couple system had been discovered and used by

Simmons[18]; a number of succinate derivatives have recently been synthesized by this method[15]. In the case of the synthesis of MB1NA, pure meso and racemic compounds were produced in 22% and 14% yields, respectively; in addition, methyl 1-naphthylacetate was identified as one of the reaction products; it was formed as a by-product by a debromination reaction which seemed to have occurred because of the steric hindrance of the bulky 1-naphthalene group at the $\beta$-position of the carboxylate group, which makes the carbon–carbon bond formation by the coupling reactions difficult, but is believed to be the major side reaction product of the coupling reaction with 30–40% yield.

The meso and racemic isomers of DM1NS were separated by recrystallization. The more symmetric meso compound which apparently has the naphthyl and ester groups in the *anti* position has the higher melting point and the larger $R_f$ value in t.l.c. as compared with the racemic isomer. The i.r. spectra of the two isomers were almost identical. The $^1$H n.m.r. chemical shift values of the meso compound are at higher field than those of the racemic isomer. A shielding of the naphthalene rings on the neighbouring protons could explain this effect because the alkyl protons of the racemic isomer are in close proximity to the naphthalene ring[19].

DM1NS was reduced in excellent yield with LAH in THF to D1NBD. The i.r. spectrum of the racemic D1NBD showed the two hydroxy groups strongly hydrogen bonded.

Replacement of the hydroxyl groups of D1NBD with bromine was achieved · with triphenylphosphine dibromide in acetonitrile according to the method developed for the preparation of $\alpha,\omega$-dibromoalkyne[20]. Dibromination with the same reagent in an attempted analogous reaction on 2,3-dimethyl-2,3-diphenylbutane-1,4-diol almost quantitatively led to the cyclic THF derivatives[21]. In our case, the bromination of mD1NBD to mD1NBD was achieved in over 95% yield; the racemic rD1NBD could also be brominated in 90% yield to rD1NDB. An intramolecular nucleophilic substitution between 1- and 4-positions to form the THF derivative was not favoured in our case, because the bulkiness of the naphthyl rings increased the strain of the THF ring that would be formed otherwise.

Grignard coupling polycondensation of D1NDB was carried out with copper(I) tris(triphenylphosphine)bromide in anhydrous THF; H-H P1VN of moderate molecular weight was obtained in relatively low yield. A number of combinations of reaction conditions, such as temperature, catalyst and solvent for the Grignard coupling polymerization, have been explored in the past[21,22], but without clear directions that could be observed. The most delicate reaction step in the Grignard coupling polymerization was the preparation of the Grignard reagent. D1NDB has acidic $\beta$-hydrogen in the 2- and 3-positions of the 2,3-substituted 1,4-dibromobutane structure; therefore the Grignard reagent was unstable and tended to undergo $\beta$-elimination to form the vinyl compound and metal hydride. The yield of polymer that could be obtained depended significantly on the physical structure and consequently the activity of the magnesium metal and the reaction temperature at which the Grignard reagent is prepared. Reactions with magnesium turnings at room temperature did not form any Grignard reagent, even when the Grignard reagent-forming modification with 1,2-dibromoethane[23] was used. At elevated temperatures, magnesium turnings were gradually consumed; no polymer was, however, formed, but only dehydrobromination was observed. When magnesium powder was used with iodine activation to initiate the formation of the Grignard reagent at room temperature[24], H-H poly(1-vinylnaphthalene) of reasonable molecular weight was obtained.

The polymer thus formed was characterized by its i.r., $^1$H and $^{13}$C n.m.r. spectra. The molecular weight of H-H P1VN was about 4600, calculated from the bromine content (based on elemental analysis) of the terminal $CH_2Br$ groups. The i.r. spectrum is in agreement with the proposed structure for the polymer, typically the absence of the absorption of the bromethyl endgroup at 1250 cm$^{-1}$ and the appearance of the absorption of a methylene group at 2980 and 3030 cm$^{-1}$. Both spectra, those of H-H and H-T P1VN, are shown for comparison (*Figure 1*).

The $^1$H n.m.r. spectrum of H-H P1VN indicated chemical shift peaks of the naphthalene ring of the 1-naphthyl group between 6.7 and 7.8 ppm, of the protons of the methine group at 2.99 ppm, and the methylene protons at 1.56 ppm. The aliphatic protons of H-H P1VN were shifted to lower field as compared with those of the H-T P1VN[25].

Grignard coupling polymerization was carried out under specific conditions by the Yamamoto method from racemic 2,3-di(1-naphthyl)-1,4-dibromobutane. H-H P1VN was obtained by precipitation into methanol in 13% yield. The methanol filtrate was concentrated under reduced pressure and the residue dissolved in benzene; the benzene solution was washed with water, sodium bicarbonate, dried, and again brought to dryness under reduced pressure. The residue was recrystallized and gave about 12% (0.13 g) of a compound of a melting point of 147–149°C; the compound was characterized by its elemental analysis, i.r. and n.m.r. spectra. From all the analytical data it is apparent that this compound was 1,2-di(naphthylcyclobutane).

The $^{13}$C n.m.r. spectrum showed two signals in the region of the aliphatic carbon atoms, one at 33.9–34.5 ppm and one at 44.4–45.8 ppm. Although the lower-field peak had been assigned to a methylene carbon in H-T poly(vinylnaphthalene)[26], the actual assignment of H-H polymer needs to be further investigated together with a more detailed study of the comparison of the physical properties of H-H P1VN with those of H-T polymer (*Figure 2*).

The u.v. spectra of H-H P1VN, H-T P1VN and D1NDB are shown in *Figure 3* and are, as expected, quite similar.

A more detailed study of the u.v. behaviour of H-H P1VN and related compounds will be reported separately.

## ACKNOWLEDGEMENTS

This work was supported in part by a grant from the American Chemical Society under PRF No. 15891-AC7 and in part by the Herman F. Mark Chair Department of the Polytechnic Institute of New York. M.N. would like to express his appreciation to Yamanashi University, Kofu, Japan, for granting him a year's leave of absence to work at the Polytechnic Institute of New York. We are greatly indebted to Mrs E. Cary for her assistance in the preparation of this manuscript.

## REFERENCES

1 Vogl, O., Malanga, M. and Berger, W. *Contemp. Top. Polym. Sci.* 1983, **4**, 35
2 Vogl, O. *J. Macromol. Sci., Chem. A* 1984, **21** (13 and 14), 1725
3 Vogl, O. and Grossman, S. *Encycl. Polym. Sci. Technol.* 1986, **7**
4 Shornigin, P. P. and Shornigina, N. V. *J. Gen. Chem.* 1935, **5**, 555
5 Frank, C. W. and Harrah, L. A. *J. Chem. Phys.* 1974, **61**, 1526
6 Irie, M., Kamijo, T., Arokawa, M., Takemura, T., Hayashi, H. and Baba, H. *J. Phys. Chem.* 1977, **81**, 1571
7 *Japan Kokai Tokkyo Koho* **82**, 108 851 (Nippon Electric Co., Ltd); *Chem. Abstr.* 1983, **98**, 15280b
8 Inoue, H., Helbig, M. and Vogl, O. *Macromolecules* 1977, **10**, 1331
9 Corley, L. S., Inoue, H., Helbig, M. and Vogl, O. *Macromol. Synth.* 1985, **9**, 31
10 Kyle, B. M. M. and Kilp, T. *Polymer* 1984, **21**, 989
11 Torkelson, J. M., Lipsky, S. and Tirrell, M. *Macromolecules* 1981, **14**, 1601
12 Lindsell, W. E., Robertson, F. C. and Soutar, I. *Eur. Polym. J.* 1981, **17**, 203
13 Yamamoto, T., Hayashi, Y. and Yamamoto, A. *Bull. Chem. Soc. Japan* 1956, **49**, 1958
14 Yamada, A., Grossman, S. and Vogl, O. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 1739
15 Grossman, S., Stolarczyk, A. and Vogl, O. *Monatsh. Chem.* 1981, **112**, 1279
16 Acton, N. and Berliner, E. *J. Am. Chem. Soc.* 1964, **86**, 3312
17 Jardine, F. H., Rule, L. and Vokra, A. G. *J. Chem. Soc. A* 1970, 238
18 Simmons, H. E. and Smith, R. D. *J. Am. Chem. Soc.* 1959, **81**, 4256
19 Jackman, L. M. and Sternhell, S. 'Applications of NMR Spectroscopy in Organic Chemistry', Pergamon, New York, 1969
20 Machinek, R. and Luettke, W. *Synthesis* 1975, 255
21 Nanasawa, M. and Vogl, O., unpublished results
22 Malanga, M. and Vogl, O. *J. Polym. Sci., Polym. Chem. Edn.* 1983, **21**, 2629
23 Pearson, D. E., Coman, D. and Beckler, J. D. *J. Org. Chem.* 1959, **24**, 504
24 Newman, M. S. and Kangan, G. *J. Org. Chem.* 1965, **30**, 3295
25 Heller, J. and Miller, D. M. *J. Polym. Sci.* (*A*-1) 1967, **5**, 2323
26 Seki, K., Mori, S. and Imamura, Y. *Bull. Chem. Soc. Japan* 1982, **55**, 2739