## ANIONIC POLYMERIZATION OF 2-VINYLNAPHTHALENE

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### Introduction

We have been interested for some time in the synthesis of macrocyclic polystyrene (PS), poly-2-vinylpyridine (P2VP) and poly-(α-methyl)styrene (PAMS)[1-3,6,7]. It was shown, for example, that PS macrocycles with molecular weights ranging from 1,660 to 70,000 and polydispersities below 1.30 had 20-30% lower hydrodynamic volumes compared to the matching linear polymers. DSC analysis showed much higher glass transition temperatures compared to the linear polymers, especially at degrees of polymerization below 50. The excimer emission for PS macrocycles was enhanced compared to the linear PS the emission of which was largely MW independent. These results stimulated our interest in the luminescence of macrocyclic polyvinylnaphthalenes (PVN) and similar polymers. [4-5]

Although there are several reports on the anionic polymerization of 2VN, they deal with kinetics of polymerization[8] or polymerizations in non-polar solvents[9-10] where coupling reactions with bifunctional electrophiles tend to be ineffective. However, in contrast to the case for 2-isopropenylnaphthalene (2IPN) in THF[11-13], no data on the MW distributions of P2VN prepared by anionic polymerization appears to have been reported.

### Experimental

**Reagents**. THF was purified first by distillation from benzophenone/Na/K and distilled subsequently from stable carbanion solutions such as the potassium salt of 1,1,4,4-tetraphenylbutane 1,4-dicarbanion. Toluene was distilled twice from $CaH_2$, then from a potassium mirror. Methanol was purified by distillation. Chlorotrimethylsilane was stirred for 24hrs over $CaH_2$ and then distilled on the vacuum line. Dibromomethane (DBM) was stirred for 24hrs over $CaH_2$ and distilled. This procedure was repeated one more time.
1,4-bis(bromomethyl)benzene (DBX) was recrystallized 2 times from chloroform and dried *in vacuo*. Then it was twice stirred in THF over $CaH_2$ and filtered.

**Initiators.** t-BuLi ('Aldrich') was sublimed under dynamic vacuum, dissolved in hexane purified over Na/K and stored in ampoules at –20°C.
K-Naph was prepared by stirring naphthalene ('Aldrich', 99%+) in THF over potassium mirror for 15-20min at 0°C and stored at -70°C.

**Monomer.** 2VN ('Aldrich', 'Alfa Aesar') was stirred for 12-16hrs in purified THF over $CaH_2$ and sublimed twice from $CaH_2$ under dynamic vacuum. THF was then distilled off, and the solid 2VN was sublimed 2 more times under dynamic vacuum, dissolved in THF and stored at -20°C in ampoules.

### Results and Discussion

Much of the starting work on the anionic polymerization of 2VN in THF was based on the results of the similar experiments[11] for 2IPN that gave high conversions after 40-60 min of polymerization time. Thus, we followed this procedure although it was known that polymerization of 2VN in THF is very rapid[8], being completed in seconds at the concentrations employed.

The non-living character of P2VN anionic species under these conditions was obvious from the beginning. Usually the polydispersities for the K-Naph initiated 2VN polymerizations in THF at -78°C were in the range 1.15-1.34 for $M_n$ values ranging from 800-8,000 (Table 1), whereas in the case of PS these values are usually below 1.10. The use of Li-Naph as initiator considerably broadened MW distributions (1.95) consistent with either slower initiation or side-reactions rapid on the polymerization time-scale. Almost complete deactivation of P2VN carbanions at higher temperatures (Table 1) was indicated by much broader MW distributions and low degrees of coupling with bifunctional electrophiles. A similar deactivation of P2IPN in THF upon warming to room temperature was described[11].

**Table 1. Polymerizations Of 2VN With K-Naph[1)].**

| Exp | K-Naph mol/l ×10³ | 2VN mol/l ×10³ | $T_p$[2)] | $DP_n^{th}$ | Polymers[3)] | | |
|---|---|---|---|---|---|---|---|
| | | | | | $M_n$ | PDI | $DP_n^{exp}$ |
| 20 | 12.5 | 85.0 | -100°C[b)] | 13.6 | 1810 | 1.23 | 11.7 |
| 6 | 13.3 | 86.7 | -78°C[a)] | 13.0 | 1103 | 1.25 | 7.2 |
| 2 | 2.9 | 97.1 | -78°C[b)] | 67.0 | 7880 | 1.34 | 51.1 |
| 17 | 12.5 | 87.5 | -35°C[a)] | 14.0 | 1609 | 1.55 | 10.4 |
| 18 | 12.5 | 85.0 | -10°C[a)] | 13.6 | 2237 | 1.80 | 14.5 |
| 21 | 12.5[4)] | 85.0 | -100°C[a)] | 13.6 | 4020 | 1.95 | 26.1 |

[1)]Conditions: one time addition of 2VN/THF to the initiator solution and stirring for [a)]1hr or [b)]30min at $T_p$; MeOH termination;
[2)]Temperature of polymerization;
[3)]SEC: 2 polystyrene-gel columns, THF eluent, 1ml/min, RI detector, polystyrene standards calibration curve.
[3)]Li-Naph is used as initiator.

Upon initiation of 2VN with t-BuLi in THF at -78°C, the polymer had narrower distributions with values of 1.10-1.20 (**Table 2**), suggesting that the wide distributions obtained for the case of the Li-Naph initiated polymerizations might be due, at least in part, to slow initiation rather than termination of the chain-end carbanion. This fact is also consistent with the relatively narrow PDI's (1.07-1.10) in the case of initiation with α-methylstyrene oligomer dianions. The incorporation of TMS groups by end-functionalization with TMS-Cl into the polymer chains clearly showed that the extent of termination increased as the higher MW polymer was formed and respective initiator concentration decreased ($<1\times10^{-2}$ M) (**Table 2**).

Reactions between P2VN, initiated with K-Naph, and bifunctional electrophiles such as DBX and DBM under conditions of multiple coupling did not give evidence of formation of high MW polymers even in the case of higher initiator concentrations ($>1\times10^{-2}$ M) and low temperatures (as low as -100°C). It is known[2] that in the case of PS, P2VP and PAMS multimodal distributions with very high (5-8 times) increases in $M_n$ are observed. However, in the case of P2VN $M_n$ values increased only by factors of 1.5-1.8 and bimodal MW distribution curves were observed. Decreasing polymerization times from 1hr to 1-2 min did not significantly improve the extent of coupling.

**Table 2. End-functionalization Of 2VN: t-BuLi Initiation, TMS-Cl Termination[1)].**

| Exp | tBuLi mol/l ×10³ | 2VN mol/l ×10³ | Polymers[2)] | | | | |
|---|---|---|---|---|---|---|---|
| | | | $M_n$ | PDI | $DP_n^{exp}$ | $M_n$[3)] | TMS[4)] |
| 7 | 10.8 | 35.0 | 674 | 1.39 | 4.4 | | |
| | | | 1537 | 1.19 | | 2830 | 95% |
| 10 | 7.9 | 85.7 | 1398 | 1.16 | 9.1 | | |
| | | | 1953 | 1.10 | | 3360 | 86% |
| 9 | 3.8 | 85.7 | 3479 | 1.18 | 22.6 | | |
| | | | 3959 | 1.11 | | 6300 | 60% |
| 8 | 1.4 | 92.3 | 10681 | 1.16 | 69.3 | | |
| | | | 10409 | 1.19 | | 14000 | 20% |

[1)]Conditions in all experiments: one time addition of 2VN/THF into the initiator solution and stirring for 1hr at -78°C;
[2)]SEC: 2 polystyrene-gel columns, THF eluent, 1ml/min, RI detector, polystyrene standards calibration curve;
[3)]$M_n$ of polymers precipitated in MeOH and dried in vacuum for 24hrs at 40°C, calculated by integration of t-Bu and aromatic region peaks of 250 MHz $^1$H NMR spectra;
[4)]TMS group incorporation calculated by integration of t-Bu and TMS peaks of 250 MHz $^1$H NMR spectra.

The nature of the deactivation may involve reaction of propagating anion with the penultimate naphthalene ring with formation of a 5-membered ring and greatly stabilized allyl/benzylic carbanions. (**Figure 1**). The nucleophilic addition of t-BuLi to naphthalene is well documented[14] and a very similar pathway was suggested[11] for the polymerization of 2IPN above 0°C. Our results indicate that for the case of 2VN in THF these reactions may operate even at -78°C. The synthesis, separation and analysis of oligomers with $DP_n$=2-4 is expected to clarify this issue.

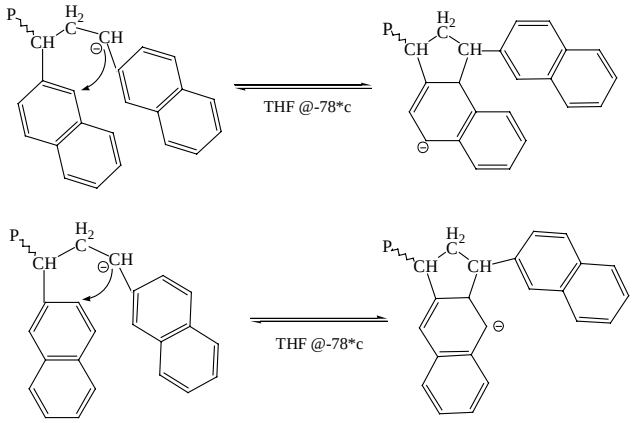


**Figure 1.** Possible side reactions in the anionic polymerization of 2VN.

It was anticipated that a less polar medium may decrease the rate of the above side-reactions. Indeed, preliminary experiments in THF/toluene mixtures gave much better results in terms of MW and MWD control as shown in **Table 3** and **Figure 2.** Thus, the t-BuLi initiated polymerizations of 2VN gave very narrow distributions that are retained on coupling with DBX and molecular weights increase by as much as 1.77 (max. 2.0). It is expected that quantitative coupling will be achieved by appropriate variation of initiator concentration and medium polarity.

**Table 3. Coupling Reactions Of Poly-2VN Anions With Bifunctional Electrophiles[1)].**

| # | t-BuLi mol/l $\times 10^3$ | 2VN mol/l $\times 10^3$ | $T_p$ | Polymers[2)] | | Electro -phile[3)] | $M_n^*/M_n$ |
|---|---|---|---|---|---|---|---|
| | | | | $M_n$ | PDI | | |
| 35 | 3.6 | 90.7 | -78°C[4,a)] | 8018 | 1.15 | MeOH | |
| | | | | 10140 * | 1.47 | DBX | 1.26 |
| 41 | 5.6 | 113.0 | -100°C[b)] | 4912 | 1.04 | MeOH | |
| | | | | 6804* | 1.13 | DBM | 1.39 |
| 42 | 4.7 | 94.2 | -100°C[b)] | 3977 | 1.05 | MeOH | |
| | | | | 7051* | 1.07 | DBX | 1.77 |

[1)]Conditions: one time addition of 2VN/THF into the initiator solution and stirring for 1-2min at $T_p$ ; [a)]THF, [b)]THF/toluene (1/3 v.v.) mixtures; coupling: dropwise addition of a coupling reagent for 3-5min at $T_p$;
[2)]SEC: 2 polystyrene-gel columns, THF eluent, 1ml/min, RI + LS detectors;
[3)]Electrophiles used: [a)]DBM – dibromomethane, [b)]DBX – α,α'-dibromo-*p*-xylene;
[4)]End-capped with diphenylethylene prior to DBX addition.

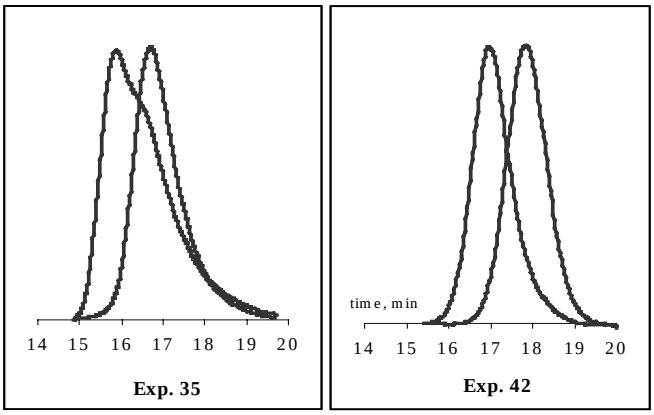


**Figure 2.** Normalized SEC traces of polymers in experiments #35 and #42.

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