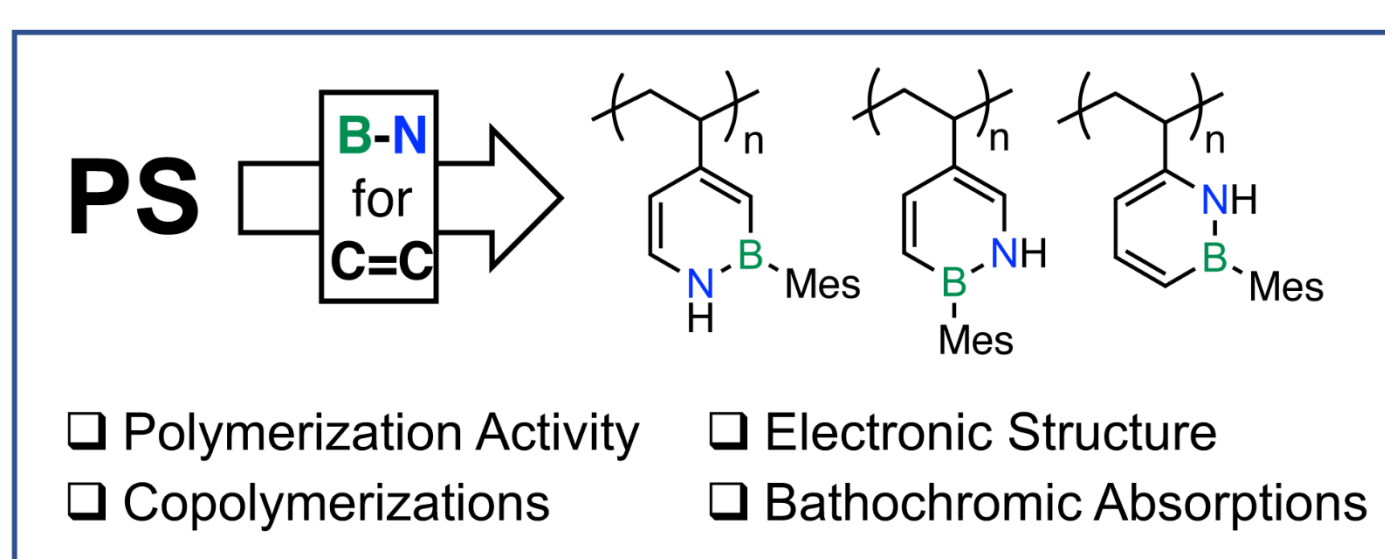


Introduction

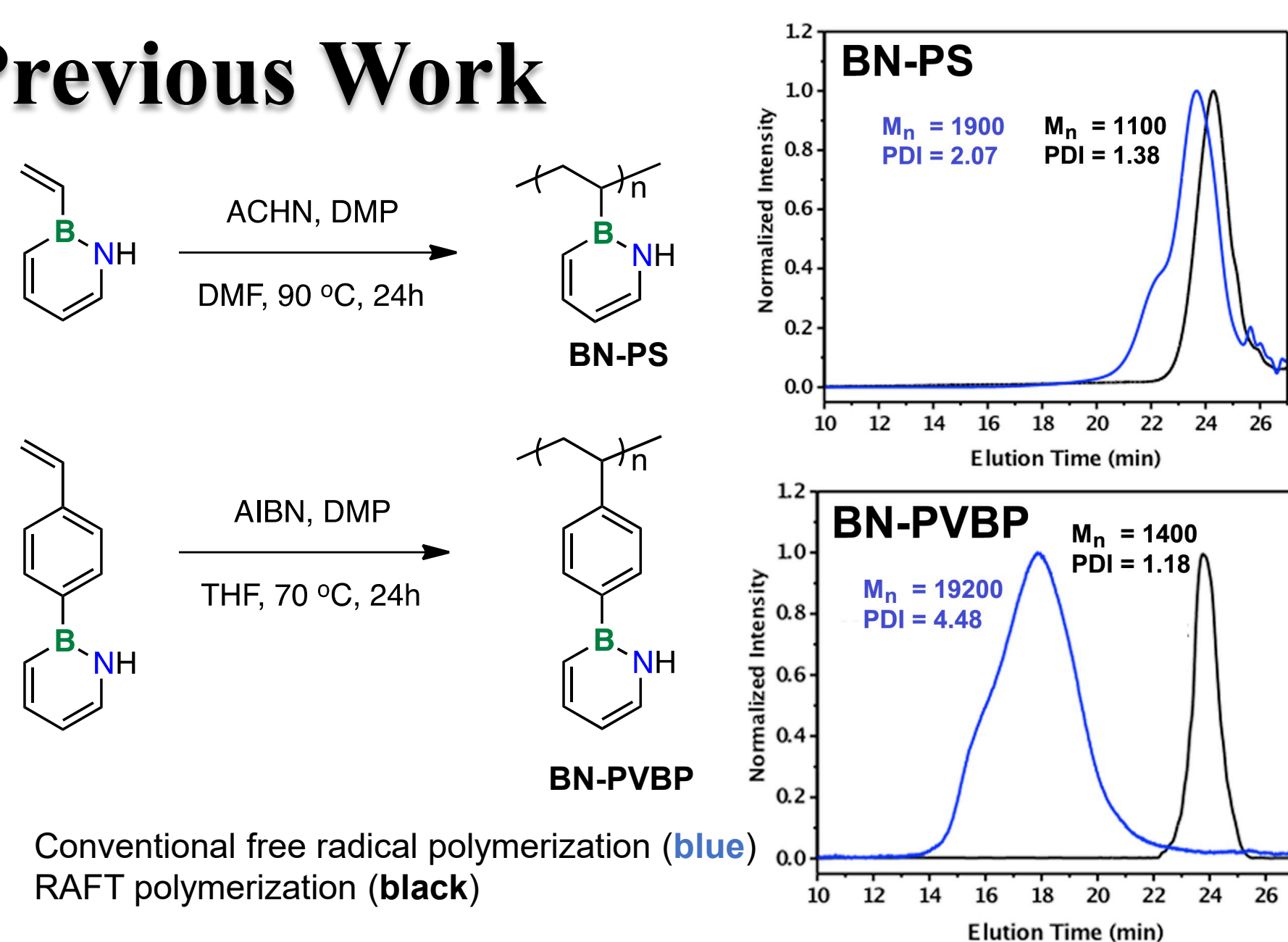
The isoelectronic and isosteric replacement of C=C for B-N units in conjugated organic systems has attracted tremendous recent interest as novel electronic properties, reactivity, and applications are achieved.¹ Fundamental studies on the replacement of ubiquitous benzene moieties for 1,2-dihydro-1,2-azaborinines, in particular, have revealed significant differences in the aromatic delocalization, whereas the polarity of the azaborinine molecule and increased acidity of the N-H proton tend to also influence intermolecular interactions.² These differences have been exploited in diverse applications.

We describe here the synthesis of a series of isomeric vinylazaborinine monomers, as well as their all-carbon counterparts. We also examine their polymerization activity in standard free radical polymerization and compare the physical properties of the resulting polymers with those of the all-carbon analogs.³

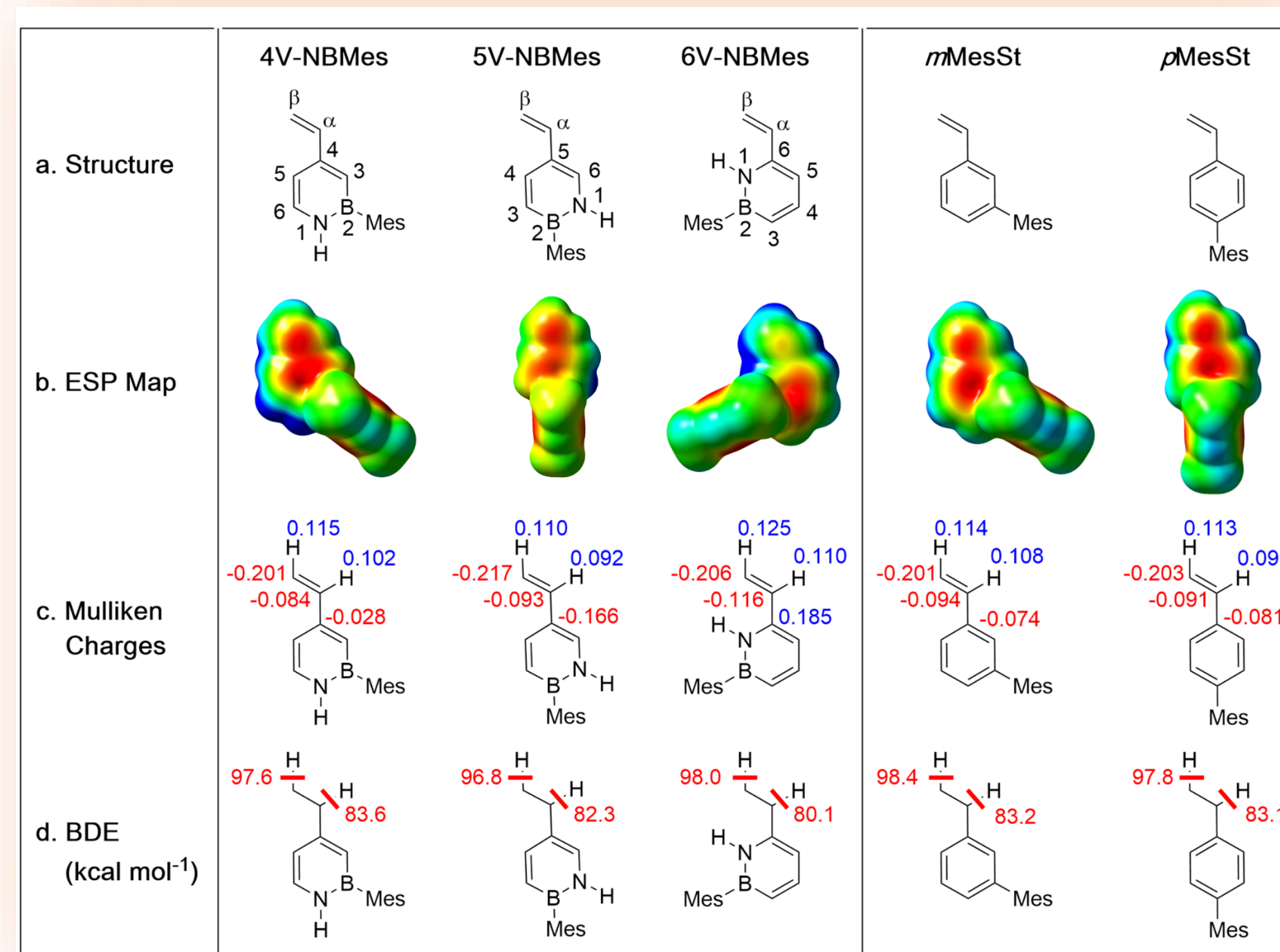


[1] A. W. Baggett, F. Guo, B. Li, S. Y. Liu and F. Jäkle, *Angew. Chem. Int. Ed.*, 2015, **54**, 11191-11195.
[2] W. M. Wan, A. W. Baggett, F. Cheng, H. Lin, A. N. Lamm, S. Y. Liu and F. Jäkle, *Chem. Commun.*, 2016, **52**, 13616-13619.
[3] H. Lin, C. McConnell, B. Jilus, S.-Y. Liu, F. Jäkle *Macromolecules* 2019, in press; DOI: 10.1021/acs.macromol.9b00466

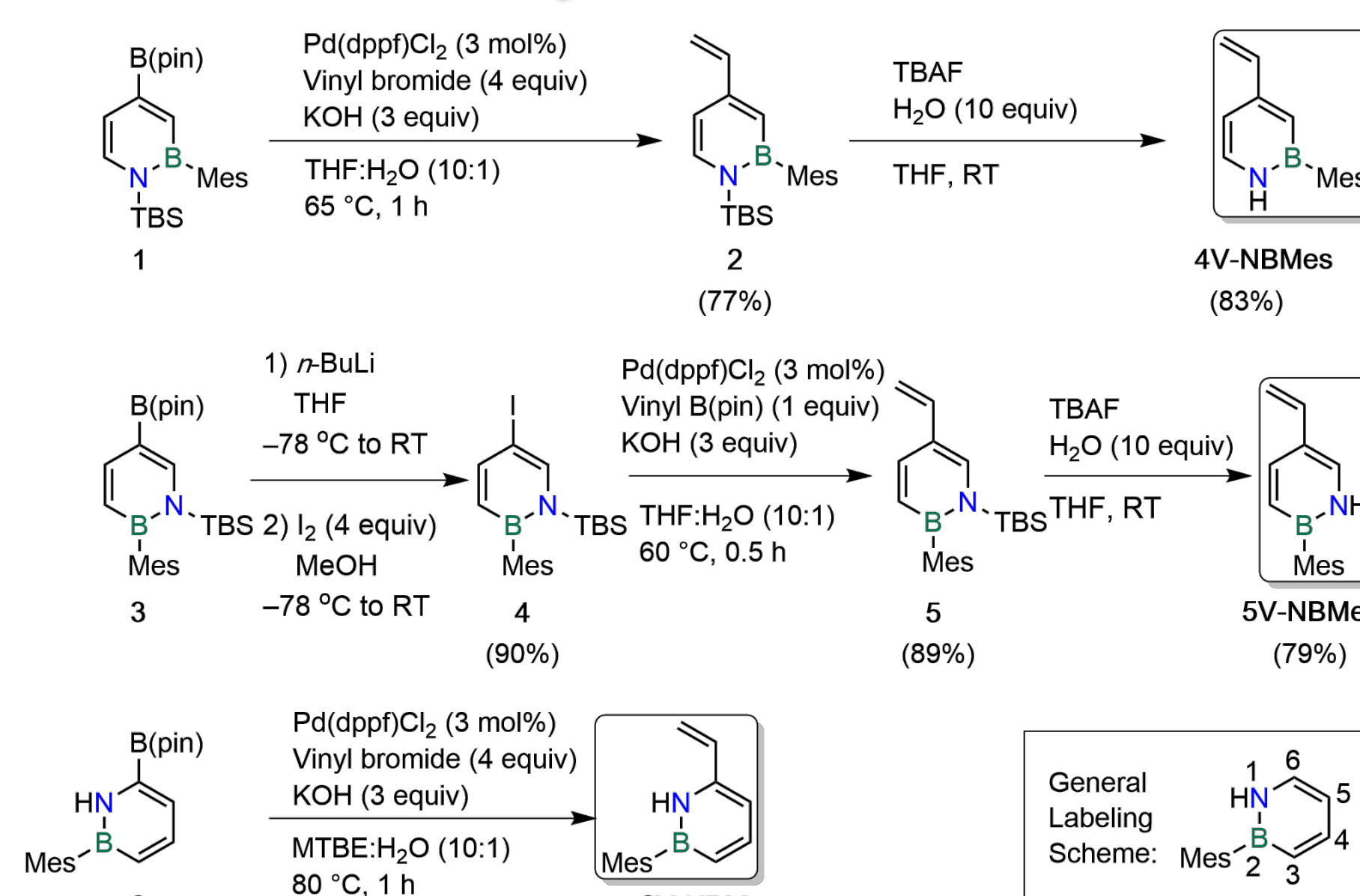
Previous Work



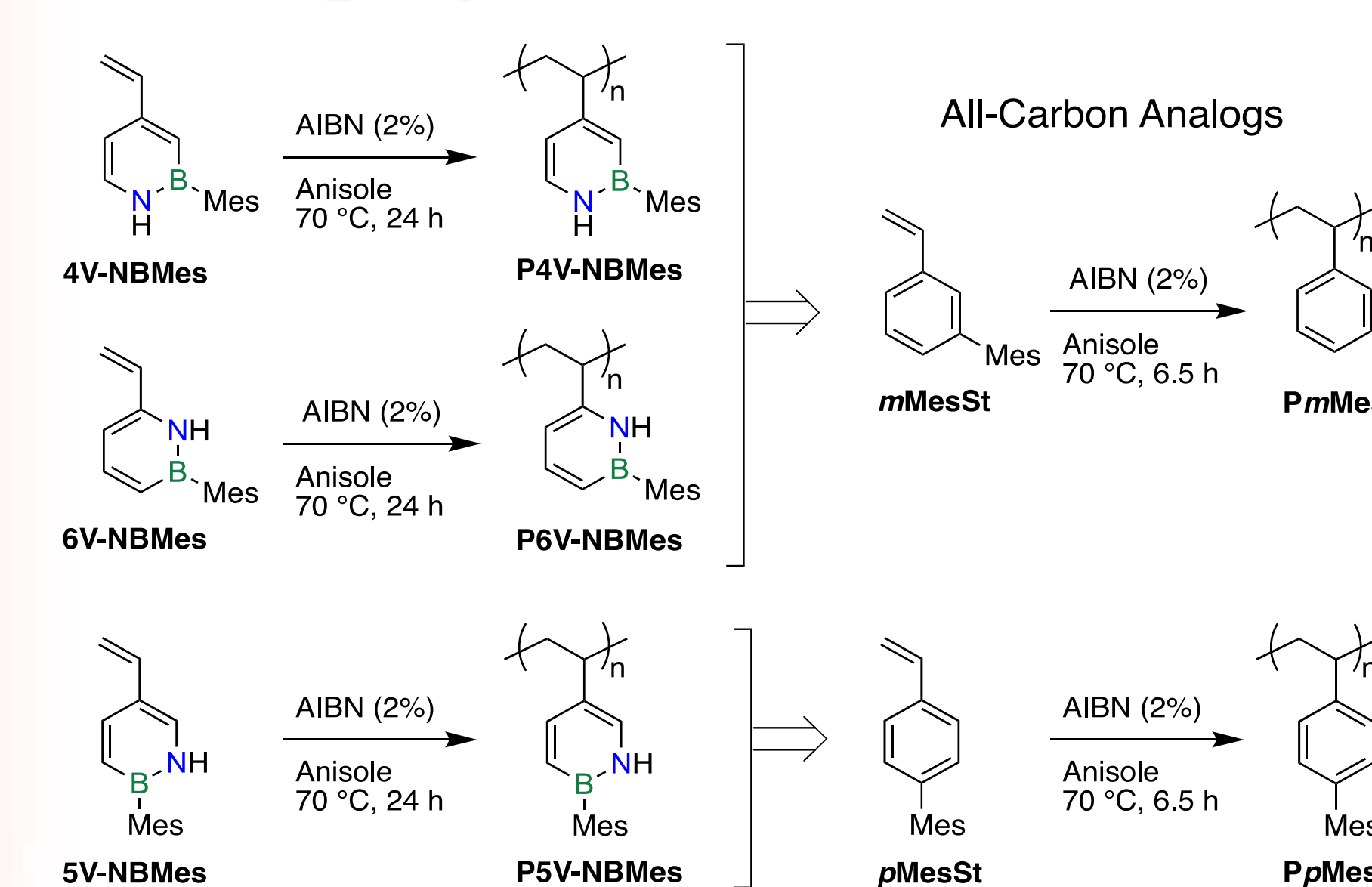
Electronic Structure Calculations



Monomer Synthesis



Homopolymerization



➤ The disappearance of the vinyl group signals and pronounced peak broadening in the ¹H and ¹³C NMR spectra indicate successful polymerization.

➤ A significant upfield shift in ¹¹B NMR spectra further confirm incorporation of the azaborinine moieties into polymers.

➤ HMQC and HMBC NMR spectra were also acquired to verify the structural integrity of the azaborinine during polymerization.

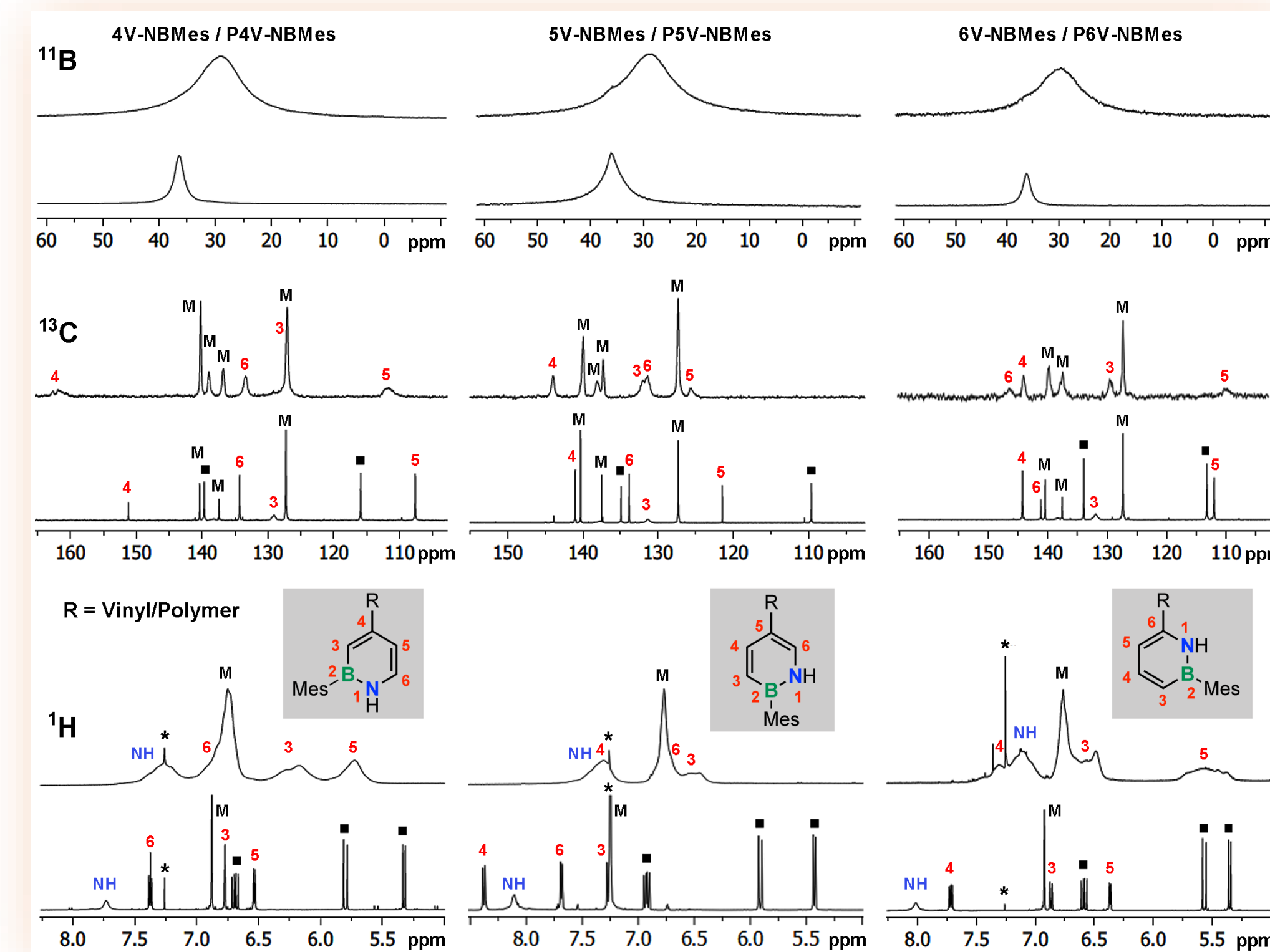


Table 1. Data for the free radical polymerization of vinyl-functionalized azaborinines and their all-carbon analogs

Monomer	Feed ratio ^a	<i>T</i> / <i>t</i> (°C / h)	Conv ^b (%)	<i>M_n</i> (kDa) ^c	<i>M_w</i> (kDa) ^c	<i>Đ</i> ^c	<i>X_n</i> ^c
4V-NBMes	50:1	70 / 24	76	26.9	130.4	4.84	119
6V-NBMes	50:1	70 / 24	51	18.2	44.4	2.44	80
mMesSt	50:1	70 / 6.5	>95	29.7	61.3	2.07	134
5V-NBMes	50:1	70 / 24	63	11.6	46.1	3.98	52
pMesSt	50:1	70 / 6.5	82	21.6	42.1	1.95	97

[a] Feed ratio of [Monomer]:[AIBN] in anisole, [M] = 4.5 M. [b] Conversion estimated based on ¹H NMR integration of residual monomer before purification relative to anisole standard. [c] Dispersity (*Đ*) and average degree of polymerization (*X_n*) based on GPC analysis of isolated product in THF relative to PS standards.

Copolymerization

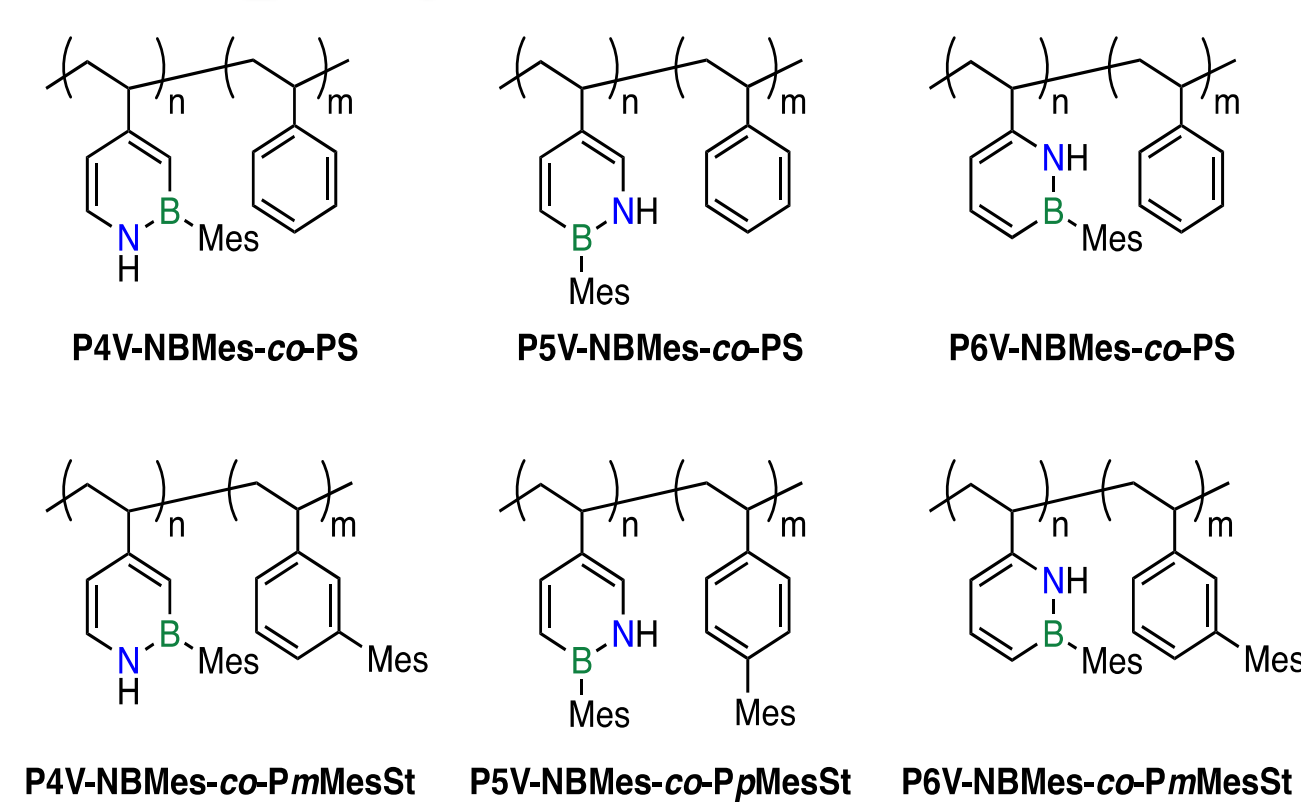
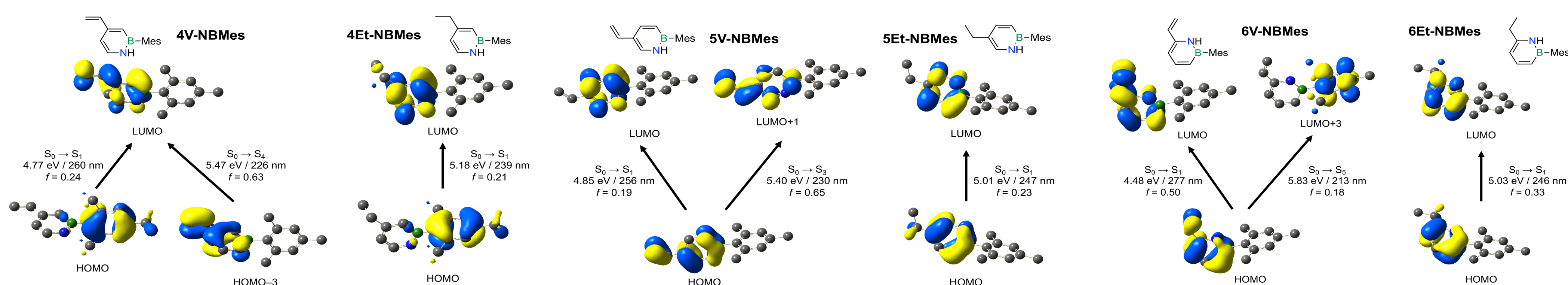
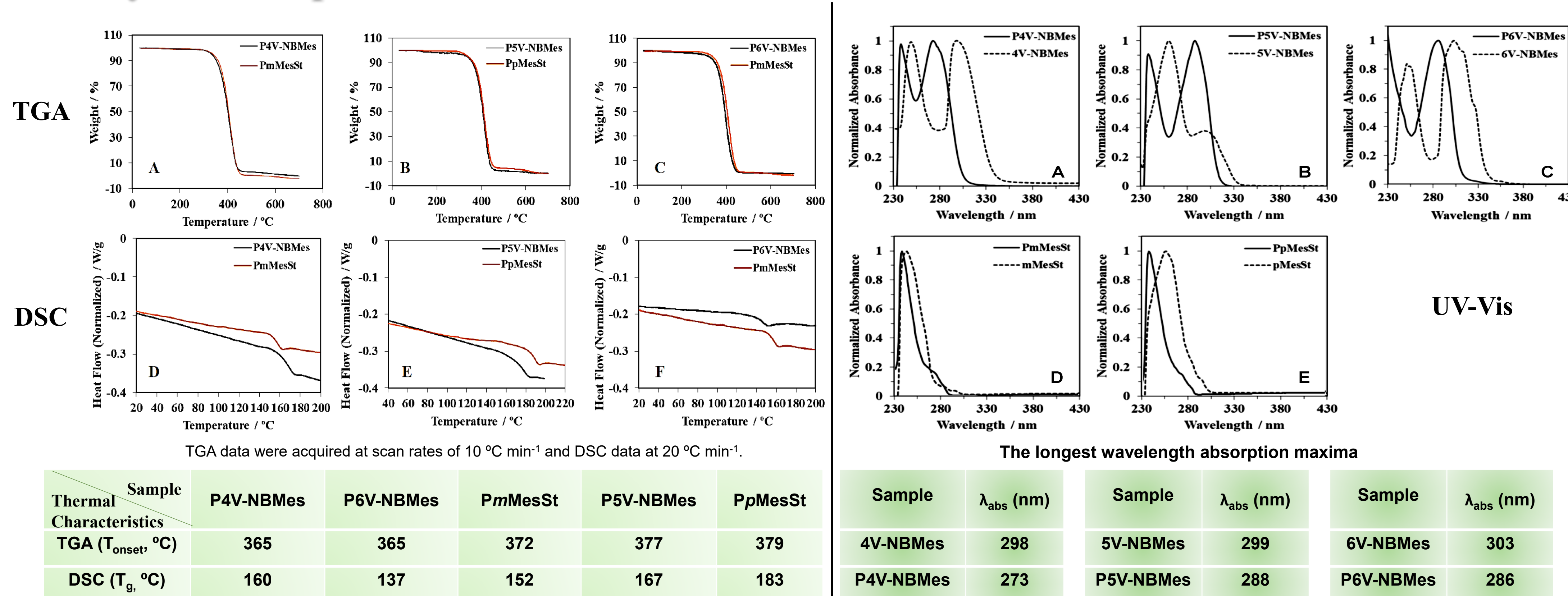


Table 2. Data for the free radical copolymerization of vinyl-functionalized azaborinines with styrene (St) and mesitylstyrene (MesSt)

Copolymer	Feed ratio ^a	<i>T</i> / <i>t</i> (°C / h)	Conv (BN) ^b (%)	Conv(St/MesSt) ^c (%)	<i>M_n</i> (kDa) ^d	<i>M_w</i> (kDa) ^d	<i>Đ</i> ^d
P4V-NBMes-co-PS	50:50:1	70 / 20	57	50	15.6	50.7	3.25
P5V-NBMes-co-PS	50:50:1	70 / 20	41	63	19.6	39.8	2.02
P6V-NBMes-co-PS	50:50:1	70 / 20	57	40	10.9	32.8	3.02
P4V-NBMes-co-PmMesSt	50:50:1	70 / 10	65	66	19.2	54.8	2.85
P5V-NBMes-co-PpMesSt	50:50:1	70 / 10	32	54	28.9	59.3	2.05
P6V-NBMes-co-PmMesSt	50:50:1	70 / 10	26	15	8.8	24.4	2.77
P6V-NBMes-co-PmMesSt	50:50:1	70 / 24	41	14	16.0	56.7	3.55

[a] Feed ratio of [BN monomer]:[Styrene]:[AIBN] in anisole, [M1] = [M2] = 2.25 M. [b] Conversion of azaborinine monomer (BN) estimated based on ¹H NMR integration of residual BN vinyl signal before purification relative to anisole standard. [c] Conversion of styrene/mesitylstyrene estimated based on ¹H NMR integration of residual styrene vinyl signal before purification relative to anisole standard. [d] Based on GPC analysis of isolated product in THF relative to PS standards.

Polymer Properties



Conclusions and Acknowledgements

- ❖ Computational studies demonstrate that the isomeric azaborinine monomers have electronically distinct structures.
- ❖ The monomers have all been successfully converted into high molecular weight polymers by AIBN-initiated standard free radical polymerization.
- ❖ Copolymerization experiments with styrene and *meta*/*para*-mesitylstyrene reveal preferential incorporation of 4V-NBMes and 6V-NBMes, but less effective incorporation of 5V-NBMes.
- ❖ The azaborinine polymers exhibit high thermal stability. The glass transition temperatures are significantly higher than for polystyrene and in a similar range as the direct all-carbon analogs derived from mesitylstyrene.
- ❖ Bathochromic shifts in absorption.

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