**PRF#: 56400-ND7**

# Amine Containing Polymers: Efficient Access to a New Family of Functionalized Materials

Dr. Laurel L. Schafer, Department of Chemistry, University of British Columbia

*Overview*

The ability to efficiently and selectively synthesize amine containing polymers is desirable due to their diverse range of applications. Such materials are often made using laborious step-wise approaches or ill-controlled post-polymerization amination. The use of 100% atom-economic catalytic methods to incorporate amines into functionalized materials is attractive for the preparation of these useful materials. Investigations in our laboratory have resulted in the development of various N,O-chelated early transition-metal (ETM) complexes that have shown good activity and functional group tolerance for the catalytic synthesis of small molecule amines via hydroamination and hydroaminoalkylation. These two complementary reactions have been used for the efficient and selective synthesis of various amines and through the successful implementation of the goals outlined in this proposal, we have developed the first catalytic approaches for the synthesis of amine functionalized polymers and oligomers to access new materials (Figure 1). Hydroamination has yielded a new class of conjugated enamine containing polymers that display unique luminescent properties. Hydroaminoalkylation has enabled the synthesis of a new class of pendant amine functionalized polynorbornene that display unique materials properties consistent with dynamic crosslinking through hydrogen bonding.

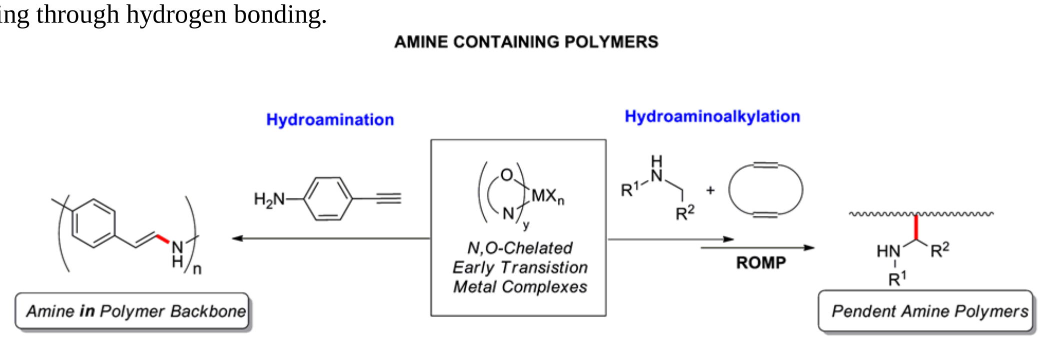


**Figure 1.** The catalytic synthesis of 2 complementary classes of amine containing polymers: 1) polymers with amines in the polymeric backbone via hydroamination and 2) polymers with pendant amine functionality using hydroaminoalkylation and ROMP.

*Research Progress*

*Hydroamination to Access Conjugated Amine Oligomer and Polymers:* The funding from PRF initiated a project on the synthesis of conjugated polyenamine materials. The success of the synthetic method was disclosed in a full paper "Ti-Catalyzed Hydroamination for the Synthesis of Amine-Containing π-Conjugated Materials"[i]. A series of conjugated enamines were prepared by Ti catalyzed anti-Markovnikov hydroamination. The synthetic route is efficient with yields of up to 94% and the 100% atom efficiency of the reaction means that these products are easily isolated and purified. Due to the extended conjugated system, the enamine tautomers were observed exclusively in both solid and solution phases, as determined by X-ray crystallography and NMR spectroscopy. These new conjugated molecules, with N incorporated into the backbone, show interesting photophysical properties including photo-luminescent quantum yields of up to 0.26. Notably, through the incorporation of B to give a donor–acceptor p-conjugated system, a redshift of approximately 100 nm is observed for the emission maximum along with the anticipated solvatochromic shifts. These synthetic methods have been extended toward the synthesis of conjugated polymers (*Manuscript In Preparation*). Notably these novel materials show unexpected luminescent properties and new materials with near IR emission have been realized. Furthermore, in related work, the oligomers were shown to be useful intermediates for preparing B-N containing heterocycles that display aggregation induced emission (*Manuscript In Preparation*). The funding from PRF was critical for initiating this new direction in my research program. The early stage results generated by my doctoral student Han Hao on this topic have formed the basis of a project for a new student that has recently joined my program. Han is now preparing to graduate in less than 5 years of beginning his PhD and he will be seeking an international postdoctoral fellowship to continue his advanced training. Han demonstrates impressive creativity and aspires to return to China for his academic career. At the moment I am looking for further funding sources to continue this research program here in Canada.

*Hydroaminoalkylation to Access Pendant Amine Functionalized Polynorbornene:* The funding from PRF also expanded the application of a family of hydroaminoalkylation catalysts toward the efficient synthesis of amine functionalized norbornene that could undergo ring-opening metathesis polymerization. The success of the synthetic method was disclosed in a full paper "Catalytic Synthesis of Secondary Amine-Containing Polymers: Variable Hydrogen Bonding for Tunable Rheological Properties".[ii] A synthetic protocol using atom-economic, catalytic hydroaminoalkylation and ring-opening metathesis polymerization (ROMP) has been developed for the versatile synthesis of a new class of aryl-substituted secondary amine containing polymers. This catalytic route minimizes waste generation and avoids protection/deprotection protocols, postpolymerization modification, and byproduct formation. Different amines can be readily incorporated to access variable hydrogen-bonding characteristics. Thermal and melt rheological characterization has shown the profound effect of hydrogen bonding on the bulk properties of these amine-containing norbornene polymers. These initial results have been followed up with further experimentation to investigate the kinetics of polymerization in order to gain insight into block-co-polymer synthesis (*Manuscript In Preparation*) and polymer molecular weight control (*Manuscript In Preparation).* These results propose key resting states that limit the catalytically active species in polymerization and point toward opportunities in monomer design to offer improved polymerization of these materials. This follow-up work also clearly demonstrates that the incorporation of hydrogen-bond donors into the polymer network results the observed unique viscoelastic properties of these novel materials. As evidence of the relevance of this new project to the petrochemical industry, I have struck a new collaboration with Shell Oil and Gas to explore these new polymers as potential anti-fouling coatings for metal surfaces. Thus, this project now continues with this new funding source and most importantly we are learning from our industrial partners about potential commercial applications of these materials. This funding supported a PDF, Sorin Rosca, to work part-time on the project, as well as 2 doctoral students Damon Gilmour and Mitchell Perry. Mitch has recently graduated and he is pursuing his PDF in the UK in the field of functionalized materials. Damon Gilmour is completing his PhD this year after 5 years of doctoral research. He aspires to shift into the polymer industry. In addition one undergraduate, Edward Tsaing, who has gone on to doctoral studies was supported by this program. Due to the industrial relevance of this work we are continuing this project and I have just had a new graduate student and a new PDF join the group to continue pushing this project forward. Here in Canada, once industrial support is identified, matching funding can be obtained through government funding programs.

*Impact on My Career* This funding from PRF has been critical for launching this new direction in my program. The preparation of these new materials were specifically cited in my recent successful nomination as a Fellow of the Royal Society of Canada, the most distinguished scholarly award for an academic in Canada. I am grateful and I continue to work to push forward on this new direction in my research group. As cited above, this grant was able to support the work of 3 graduate students and a ½ of the work of a PDF in addition to an undergraduate researchers. By the time all of the papers are completed this funding will have supported in part a minimum of 6 publications and perhaps more! I have been able to translate these results into an on-going industrial collaboration to continue funding this research. Through these fruitful collaborations I have been able to learn a lot about this new area of science; functional and responsive materials. This funding was timely and critical to expand the work of my group in this new direction toward materials science.

---

[i] Hao, H.; Thompson, K. A.; Hudson, Z. M.; Schafer, L., Ti-Catalyzed Hydroamination for the Synthesis of Amine-Containing π-Conjugated Materials. *Chemistry – A European Journal*, **2018**, *24*, 5562-5568.

[ii] Perry, M. R.; Ebrahimi, T.; Morgan, E.; Edwards, P. M.; Hatzikiriakos, S. G.; Schafer, L. L., Catalytic Synthesis of Secondary Amine-Containing Polymers: Variable Hydrogen Bonding for Tunable Rheological Properties. *Macromolecules,* **2016,** *49*, 4423-4430.