A Study of the Scope, Limitations and Kinetics of the Siliconization of Triarylamines Using Tris(pentafluorophenyl)borane Catalysis.

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Abstract

Piers-Rubinsztajn (P-R) conditions, involving catalysis by tris(pentafluorophenyl)borane, were applied to siliconize triarylamines. A phenylated linear methylhydrosiloxane copolymer was utilized to create a hydrolytically-stable composite with promising optical, electrochemical and thermal properties. However, the reaction was highly exothermic, had rapid uncontrollable kinetics and produced methane as a byproduct; problematic characteristics for larger scale syntheses. Thereafter, triarylamines with bulkier substituents were studied to determine whether the kinetics could be slowed and a less volatile byproduct created. The rate of conversion was retarded significantly as expected, but not all derivatives reacted quantitatively in ambient conditions. Finally, P-R conditions were applied to methylhydrosiloxane-dimethylsiloxane copolymers. Gelation in air upon extended reaction time was effectively avoided by “finishing” excess Si-H sites using anisole. The result was the preparation of composites with up to 61 wt % arylamine content, which are expected to have significant applications as cost-effective flexible hole transport layers in organic electronic devices.
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Introduction

This chapter is an assembly of the introductions originally written for chapters 2 through 4. Scheme 2 was created by Prof. Tim Bender (Dept. of Chemical Engineering & Applied Chemistry, University of Toronto) and Scheme 3 was expanded by him; everything else was written/made by me.

Throughout this document the nomenclature established by General Electric will be adopted, with ‘*’ indicating Si-H functionality, ‘M’ denoting a silicon atom with one oxygen attached, ‘D’ denoting a silicon atom with two oxygen atoms attached, and ‘T’ denoting one with three attached. The words “hydro”, “hydrogen” and “hydrido” in the context of silicones are used interchangeably to denote hydride functionality at silicon. The terms “silicone” and “siloxane” are also considered equivalent. Finally, the numbering systems used for starting materials, reagents and products are unique to each chapter: self-consistent within the chapter but repetitive between chapters.

1.1 Arylamine pendant polymers

Our group has been active in the development of soft functional materials for organic electronics based on siliconization of triarylamines, carbazoles, and two-centered tetraaryl-biphenyldiamines and tetraaryl-phenylenediamines.¹ These molecules, collectively known as arylamines, are a well-known class of hole-transporting materials (HTMs).²,³ Our siliconized arylamines are liquids or waxes and we have shown them to be organic semiconductors.³ We have thus coined the term LOSs (liquid organic semiconductors). Often, as small molecules, HTMs are incorporated in organic electronic devices as thin films using vacuum deposition techniques. However, solution processing methods, such as inkjet printing, hold particular advantages in the

production of uniform layers across large areas.⁴ As a set of manufacturing techniques, there are several solution-based processes available, such as gravure, flexographic and screen printing; knife and slot-die coating; printing and spray coating.⁵ These are expected to be much less expensive and less energy-intensive, while also being amenable to higher throughput, than current spin coating and batch vacuum deposition methods.⁵c Further applications in organic electronics would thus be enhanced by facile, orthogonal processability from solution while maintaining or improving the charge carrier mobility of these materials, which are generally crystalline solids at room temperature. Incorporating a triarylamine into the structure of a flexible polymer is recognized to provide better film-forming properties from solution.⁶ For example, a polymeric version of a fluorinated triphenyldiamine, made by polymerization of a constituent vinyl group, showed similar or better performance in an organic light-emitting diode (OLED) than the small-molecule analogue.⁷ The incorporation of a triarylamine pendant to poly(methylhydrosiloxane) (PMHS) was also found to produce a silicone–triarylamine hybrid polymer with hole-transporting properties comparable to the respective small molecule.⁸ Similar results were observed for polymers containing the related carbazole group.⁹

Siliconized charge transport materials may show improved interfacial properties in a multilayer device. Introducing an ultrathin surface wetting layer improved the fill factor and, thus, efficiency of an organic solar cell; an OLED showed analogous performance enhancement with a siliconized hole injection/transport interlayer. Researchers have grafted moieties with complementary optoelectronic behaviour to the same polymer backbone;⁹¹⁰,⁸ polymers thus functionalized with a sequence of HOMO energy levels enabled higher efficiency in sought-after

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deep blue-emitting\textsuperscript{11} OLEDs.\textsuperscript{12} In addition, siliconized charge transport materials showing liquid-crystalline self-assembly have the potential for higher charge carrier mobilities. Furthermore, composites with greater mechanical flexibility than the component crystalline small molecules may enable new innovations in lighting and organic photovoltaics (OPVs): for example, by forming the material into morphologies for more efficient photon collection or outcoupling.\textsuperscript{5b} Silicone resins can be made with high transparency as well as resistance to UV, heat, oxygen and water degradation;\textsuperscript{13} the latter two are some of the major factors limiting performance lifetime of organic electronic devices.\textsuperscript{14} Regardless of the method, then, there is a clear and demonstrated desire to form flexible polymers with pendant triarylamine functionality, and the utility of such materials has been demonstrated. We are therefore interested in alternative, straightforward and versatile chemical pathways to prepare arylamine functionalized polysilicones.

1.2 \textbf{Pendant polymerization techniques and relevant silicon chemistry}

There are several examples of both conjugated and non-conjugated oligomers and polymers pendant functionalized with arylamines or their derivatives. In addition to the direct polymerization of vinyl-containing triarylamines,\textsuperscript{15} post polymerization grafting techniques have been used extensively to form triarylamine-containing polymers.\textsuperscript{9} The most common technique involves silylative coupling methods such as hydrosilylation of vinyl,\textsuperscript{16,10} allyl,\textsuperscript{16c,d,17} or ethynyl\textsuperscript{18}


groups attached to a triarylamine or carbazole derivative with silanes (Si–H) using hexachloroplatinate(IV) hydrate, Karstedt's catalyst or other Pt- or Ru-based catalysts. For example, Belfield et al. and the groups of Moerner and Siegel and co-workers have attached N-allylcarbazoles and an allyl-functionalized triarylamine, respectively, to poly(methylhydrosiloxane using hydrosilylation to synthesize new photorefractive polymers. The former group found the resulting polymer to be soluble in a broad range of solvents including CH₂Cl₂, CHCl₃, CH₃CN, THF, and DMF. Another method for the formation of pendant triarylamine silicone polymers involves the use of organometallic reagents, such as Grignard or halolithium triarylamines, which are reacted with chloro- or alkoxysilanes. However, these reactions are susceptible to several side reactions and known to create byproducts. It is presumed that if the metal species remains in the final polymer, it will result in charge trapping, unbalanced carrier transport, or nonradiative recombination, all of which are generally detrimental to performance of organic electronic devices.

The formation of Si-O bonds is of great importance in the silicones industry as well as in materials and protecting group chemistry. Traditionally, this is achieved using one of two

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19. Waehner, J.; Marciniec, B.; Pawluć, P. Eur. J. Org. Chem. 2007, 2975–2980. Synthetic routes other than hydrosilylation continue to be used, such as this Ru-catalyzed silylative coupling but, based on a literature search, this technique is still less common than hydrosilylation.


common methods. The first is typically utilized to form a silyl ether as a protecting group during a multistep chemical synthesis. The reaction involves the action of a nucleophilic hydroxyl group on a mono-functional chlorosilane producing the silicon-oxygen bond (silyl ether) and a stoichiometric amount of hydrogen chloride (as a byproduct).\textsuperscript{24} This reaction is limited by the availability of the respective mono-functional chlorosilane, and may be ineffective with tertiary or other hindered alcohols.\textsuperscript{25} The second method, the so-called sol-gel method, also involves chlorosilanes (but typically ones which are multifunctional) or alkoxy silanes which are hydrolyzed in the presence of water and either acid or base catalyst. The resulting silanols self-condense to produce Si-O-Si bonds and ultimately silicones (either linear or crosslinked).\textsuperscript{26} Less common are methods involving the use of metal catalysts that accomplish the dehydrocoupling of silanes with alcohols.\textsuperscript{27}

1.3 **Piers-Rubinsztajn chemistry**

Tris(perfluorophenyl)borane (B(C$_6$F$_5$)$_3$, hereinafter BCF) is a sterically hindered strong Lewis acid that found early applications as a cocatalyst activator in metallocene-based polymerizations of $\alpha$-olefins, and has since been used in inorganic, organometallic and organic chemistry.\textsuperscript{28} Although highly hygroscopic, it shows good water and air stability\textsuperscript{29} and is a nonvolatile solid at SATP. As discussed above, we are interested in forming covalent linkages between siloxanes and arylamines. As illustrated in Scheme 1, BCF is active toward two main classes of reactions that accomplish this. The first to be discovered was the reduction, with a silane (or dihydrogen,\textsuperscript{30} not discussed here), of a multiple C=X bond (X = O, N, some S and C), \textit{i.e.} hydrosilylation.\textsuperscript{31}


Scheme 1: Silicon-heteroatom bond forming reactions catalyzed by BCF. Upper reactions are Piers-Rubinsztajn chemistry (R₁ to R₃ any non-basic functional group, R₄ = alkyl, aryl, silyl, R₅ = alkyl or H). Lower reactions are hydrosilylation.

The second type of reaction is condensation of a C-OH, C-O-R, Si-OH or Si-O-R group (R = alkyl or aryl) with an Si-H moiety, i.e. cross-dehydrocoupling or dehydrocarbonative coupling, which forms an Si-O-Si or Si-O-C bond. This more recently discovered Piers-Rubinsztajn reaction, or Piers-Rubinsztajn conditions, were elucidated and explored by boron²⁸a and silicon/polymer³³ chemists, and have been utilized by both groups for installing silyl ether protecting groups, in organic reductions, and in facile syntheses of stereoregular and other well-defined siloxane architectures. The reaction’s name derives from two researchers, Warren Piers (University of Calgary, Canada) and Sławomir Rubinsztajn (General Electric, USA), who contributed largely to elucidating the relevant mechanistic details. The catalytic mechanism relies on activation of the Si-H bond, forming a polarized Si—H..BCF complex (Scheme 2). This weakly-stabilized species may undergo an S₈₂-Si reaction with ethers, alcohols, silanols, ethers and some thiols. A final, rapid hydride transfer leads to either

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regeneration of the starting materials, metathesis, or the desired silylation of the nucleophile with H₂ or the R-group hydrocarbon released as a byproduct (Scheme 3). Thus, in the final step of the mechanism, dehydrocarbonation (or redox condensation) competes with a metathesis that results in exchange of the two functionalities: \( ^{31d} \)

\[
R_3SiOR' + R''_3SiH \xrightarrow{B(C_6F_5)_3} R''_3SiOR' + R_3SiH
\]

Chojnowski et al. suggested that alkoxy substituents with secondary C will interact more favourably with soft H' than will harder primary C, shifting the final step more toward condensation over metathesis.\(^{31d}\) In fact, the latter process can be effectively suppressed for certain reaction conditions and reagents.\(^{13,39}\)

Scheme 2: Activation of silane with BCF and the resulting generalized compounds made on reaction with a variety of nucleophiles (Piers-Rubinsztajn conditions).


P-R conditions are both versatile and rapid; for example, a 2600 g.mol\(^{-1}\) discrete siloxane has been synthesized in two steps within 75 min at 60°C, in >90 % yield;\(^{39}\) polymerization of bisphenols with 1,1,3,3-tetramethyldisiloxane or 1,4-bis(dimethylsilyl)benzene was completed in less than 1 h;\(^{43}\) and our group has shown that we can use P-R conditions to install discrete\(^1\) or polymeric silicones\(^{44}\) onto triarylamine substrates. BCF side reactions with the nucleophile or other Lewis bases,\(^1\) including water, sequester it from catalyzing the P-R reaction.\(^{42,45}\) Zhou and Kawakami observed that the cross-dehydrocoupling of short dihydrosilanes and disilanols gave optically pure polymer in high yield in toluene but not in polar nonaqueous solvents.\(^{38}\) This may be connected to findings of Bergquist\(^{\text{et. al.}}\) that BCF forms a Brønsted acid in the presence of water (strength comparable to HCl in acetonitrile), and that the B-L association for L = H\(_2\)O is more labile than for L = MeCN (200-fold difference in dissociation rate constant).\(^{46}\) When traces of water are present in solution, the Lewis acid form of BCF tends to eliminate it by catalyzing silation to form silanols, which may couple with another silane. At low (~1 mol \%) concentrations of BCF, the P-R reaction is compatible with alkenes, some acyl groups\(^{47}\) and haloalkanes.\(^{25,48}\) At higher (2–5 wt \%) catalyst loadings, vinyl groups will also be partially reduced by the Si-H species,\(^{49}\) and excess poly(methylhydrosiloxane) will fully deoxygenate a variety of ketones and aldehydes.\(^{36}\)

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It has been shown computationally and experimentally that the equilibrium between catalyst-hydrosilane and free catalyst favours the latter.\textsuperscript{50} Parks and Piers originally found that more Lewis-basic substrates are discriminatively hydrosilylated in the presence of less basic ones, but the reaction rate is actually higher for less basic substrates. Excessive Lewis basicity, as with unhindered amines, will irreversibly complex the catalyst and shut down the P-R reaction pathway. It seems that a balance of sufficient nucleophilicity and low-enough Lewis basicity, then, is required to achieve the desired reaction. We have found triarylamines sufficiently hindered and weak as Lewis bases that they do not fully quench BCF’s activity and, therefore, arylamine methyl ethers can be used to functionalize siloxanes using mild conditions, making an Si–O–triarylamine bond with the elimination of CH$_4$ as a byproduct.\textsuperscript{1}

1.4 Kinetics of P-R chemistry

Kinetics of the Piers-Rubinsztajn reaction have been studied in both dry and aqueous systems. In their elucidation of the P-R reaction mechanism and kinetics, Piers, Chojnowski, Rubinsztajn and coworkers observed a few key points. With primary leaving group, the kinetic rate law was termolecular in nature after the initial formation of the activated silane-BCF pair (coordinated silylium).\(^{42}\) In the absence of water, for alkoxy silanes, the reaction rate depends linearly on (initial) BCF concentration and is first-order in Si-H and Si-OR functionalities (R'-OR type structures were not investigated):

\[
-k = k \left[ \text{BCF} \right] \left[ \text{SiH} \right] \left[ \text{SiOR} \right].^{31d}
\]

For mechanistically similar BCF-catalyzed hydrosilylations of C=O and C=N functional molecules, conversion is much slower for greater steric bulk around either the Si atom or the nucleophile (analogous to the silane and ArOR\(_3\) in Scheme 3).\(^ {31b,42}\) More recently, Rendler and Oestreich showed conclusively that the BCF-catalyzed hydrosilylation involves an S\(_{N2}\)-Si displacement of the hydride group from silicon by the nucleophile. The experiment in question utilized the prochiral ketone acetophenone and an enantioenriched (90% ee) silane; inversion of sterochemistry at the chiral Si centre was 97%.\(^ {30}\) In an S\(_{N1}\)-Si mechanism with, for example, hydride abstraction by BCF separately from the nucleophilic attack, the resulting silylium ion would spontaneously rearrange to a planar geometry around Si, rendering it achiral and leading to racemization of the product. The near-absence of racemization, then, supports a concerted mechanism for the rate-determining step of the analogous P-R reaction as well, which also requires all three of the borane, silane (in a B--H--Si quasilinear complex shown in Scheme 3) and nucleophilic O species. Sterically-caused retardation of the rate of S\(_{N2}\) reactions is well known.\(^ {52}\) Simulations have shown a high \(\Delta S^f\) and low \(\Delta H^f\) for this nucleophilic attack on the silane by the ether,\(^ {31d}\) further substantiating the reasoning that steric effects will retard the reaction rate.

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1.5 Control of P-R chemistry for practical applications

We have applied P-R conditions to functionalize methoxylated arylamines with oligosiloxanes. Based on our knowledge of the kinetics and mechanism of the reaction, we hypothesized that steric effects could be utilized to control conversion rate of our arylamine precursors. The significant exotherm, rapid reaction rate and rapid release of volatile and flammable byproducts (hydrogen or low molecular weight hydrocarbons) in the reactions described is a potentially hazardous concoction of conditions, particularly at larger scales. It is therefore of interest to study ways in which the hazards can be mitigated. As changes to the chemical structure of the silane (increasing its bulk) would result in the formation of distinctly different siliconized triarylamines we elected to study the potential of using triarylamine substrates with leaving groups which were more bulky and, therefore, less volatile. Catalyst concentration also directly affects reaction rate, but at low charges ($< \sim 10^{-3}$ mol.kg$^{-1}$) BCF is sensitive to inhibition by alcoholic and other weakly Lewis basic species as noted above.

We thus chose to focus on three leaving groups of different sizes: methyl, butyl and benzyl. Both methyl and butyl form methane and butane (volatile gases at STP) whereas benzyl is both bulkier than butyl and simply forms toluene, the reaction solvent, as a byproduct. We synthesized three triarylamine model compounds (1a-c, Scheme 3, Chapter 4) and compared their reactivities with a series of structurally varied hydridosiloxanes including pentamethyl disiloxane; 1,1,1,3,5,5,5-heptamethyl trisiloxane; a short 2100 g.mol$^{-1}$ silicone copolymer, poly(dimethylsiloxane-co-methylhydrosiloxane) (PDMS-co-PMHS, denoted poly-M) with trimethylsilyl (M) end groups and 4 Si-H (D*) units per chain; and a commercial dimethylhydrosilyl-terminated poly(methylphenylsiloxane)-PMHS copolymer (PMPS-PMHS, denoted poly-Ph) with 45 – 50 mol% specified Si-H functionality.

Given the utility outlined above for silicone–triarylamine hybrid polymers, it was of interest to see whether the scope of P–R conditions can be extended past the use of simple small discrete silicone fragments, to the preparation of polysilicone–triarylamine composites where triarylamine is pendant to the flexible main chain. Therefore, in the following chapters, the application of P–R conditions to install model triarylamines pendant to phenylated and methylated siloxane copolymers are described, along with limitations encountered. The physical

properties of the triarylamine moiety before and after grafting to the silicone are compared, and the robustness of the reaction conditions and stability of the products are discussed. With respect to future applications of these materials in organic electronic devices such as OLEDs and OPVs, there are several properties of such a hole transport layer (HTL) important for good device performance, such as transparency, surface uniformity, and resistance to erosion under the conditions of deposition of the next layer. The latter condition can be met by utilizing thermal or photo-crosslinking treatments to change the HTL’s solubility in situ.\textsuperscript{55} It can also be met by utilizing an orthogonal solvent, such as hexamethyldisiloxane (MM), which dissolves virtually no other organic electronic material. This way, arylamines can be deposited in such a layer-by-layer process without disturbing or eroding the underlying organic layer.

Two more materials properties are significant in enabling the widest range of applications in flexible organic electronic devices. Firstly, the arylamine-silicone composite must have a certain minimum content of electronically active arylamine, known as the percolation threshold,\textsuperscript{56} to accomplish successful charge transport through a layer of the material. This threshold is expected to lie in the vicinity of 30 vol. % for our composites, but may be as low as 10–20 vol. % depending on the morphology and microphase behaviour of the polymer chains.\textsuperscript{57} Secondly, the final materials should be either glasses, liquids or waxy solids throughout the range of terrestrial temperatures likely to be experienced by a device: approximately -30°C to +50°C. Thus, the glass transition temperature, $T_g$, of the composite HTL should lie outside of this range.

\section*{1.6 Thesis Statement}

Piers-Rubinsztajn chemistry, using the catalyst tris(perfluorophenyl)borane, can be utilized to produce triarylamine pendant silicone copolymers from a variety of silicones in order to tune the physical properties of the material while maintaining the favourable optoelectronic properties of the triarylamine. The rate and byproducts of the reaction can be controlled within a useful range by changing the leaving group of a triarylamine ether or the steric environment of the hydridosilicone.


2
The Use of Piers–Rubinsztajn Conditions for the Placement of Triarylamines Pendant to Phenylated Silicone Polymers

This chapter is taken from a published paper: Gretton, M.J.; Kamino, B.A.; Brook, M.A.; Bender, T.P. *Macromolecules*, 2012, 45, 723–728. The synthesis of arylamines 1 and 2 was performed by me in consultation with Brett Kamino (Dept. of Chemical Engineering & Applied Chemistry, University of Toronto), and the discussion of reactions summarized in Table 1 was expanded by Prof. Timothy Bender. Mohsen Soleimani, at the time a Ph.D. candidate in the group of Prof. Mitchell Winnik (Department of Chemistry, University of Toronto), performed the DSC measurements. All other syntheses, materials characterizations and measurements were performed by me.

2.1 Results and Discussion

The synthetic route used to construct the model triarylamine 2 is outlined in Scheme 4. The synthesis of 2 was accomplished by reaction of 3,4-dimethylaniline with 4-bromoanisole to form the intermediate diarylamine (1) under standard Buchwald–Hartwig coupling conditions. Further reaction of 1 with 4-bromobiphenyl, again under standard conditions, gave the model triarylamine 2 in good yield and purity. Triarylamine 2 contains the reactive arylmethoxy unit that is necessary for participation in the P-R coupling reaction. It also contains both 3,4-dimethylphenyl and biphenyl molecular fragments. These were chosen because of their presence in the triarylamine, bis(3,4-dimethylphenyl)-(1-biphenyl)amine whose electronic properties, including oxidation potential and charge carrier mobility are known.

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Scheme 4: Synthesis of triarylamine 2 followed by grafting onto silicone polymer under Piers-Rubinsztajn conditions to produce silicone-triarylamine hybrid polymer 3. CH₄ byproduct of the reaction is not shown.

A silicone polymer was then selected for reaction with the triarylamine 2. The silicone selected was HPM-502 of Gelest Inc., a silicone copolymer of moderate viscosity containing both methyl-hydride (45-50%) and methyl-phenyl units with a hydride terminus. A silicone polymer containing phenyl units was chosen to ensure compatibility/cosolubility of the silicone polymer and the triarylamine at ambient temperatures in toluene (the solvent of choice for P-R reactions on triarylamines). Furthermore, qualitatively the presence of phenyl units should ensure the polymer adopts a largely extended uncoiled conformation in solution thus making the hydride functionality available for reaction. By comparison, poly(dimethylsiloxane) is expected to adopt a coiled conformation in toluene solution owing to its unfavorable $\chi$-parameter (0.802). If we extend this to the structurally related methyl-hydride/dimethyl siloxane copolymer the hydride groups would potentially be unavailable for reaction due to a likely coiled conformation in solution.

Initial reaction of HPM-502 with 1.1 equiv of triarylamine 2 (relative to hydride) at a solution concentration of 25 wt% resulted in incorporation of only 53% of the triarylamine into

---

the polymer, leaving 40% of the original hydrides (Si-H) remaining in the polymer (i.e. 60% reacted, run 1, Table 1). The percent incorporation of the triarylamine in the polymer was calculated based on comparison of areas of the resolved polymer and triarylamine peaks in a GPC chromatogram (extracted from a PDA chromatogram at 330 nm, a wavelength specific for the triarylamine chromophore) with the assumption of similar molar absorptivities of free and pendant triarylamine moiety. Chromatograms of the product 3 and HPM-502 are given in the Electronic Supporting Information accompanying this article (Figure S1).

Table 1: Summary of reactions of silicone copolymer with triarylamine 2 under Piers-Rubinsztajn conditions.

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature (°C)</th>
<th>Weight% solids (±1%)</th>
<th>Molar equivs triarylamine (±0.02)</th>
<th>%Conversion of triarylamine</th>
<th>%Conversion of Si-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>rt</td>
<td>25</td>
<td>1.1</td>
<td>53</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>rt</td>
<td>25</td>
<td>0.9</td>
<td>69</td>
<td>62</td>
</tr>
<tr>
<td>3</td>
<td>rt</td>
<td>20</td>
<td>0.9</td>
<td>60</td>
<td>54</td>
</tr>
<tr>
<td>4</td>
<td>rt</td>
<td>15</td>
<td>0.9</td>
<td>44</td>
<td>39</td>
</tr>
<tr>
<td>5</td>
<td>55</td>
<td>25</td>
<td>0.9</td>
<td>66</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>80</td>
<td>25</td>
<td>0.9</td>
<td>66</td>
<td>59</td>
</tr>
<tr>
<td>7</td>
<td>rt</td>
<td>25</td>
<td>0.6</td>
<td>82</td>
<td>48</td>
</tr>
<tr>
<td>8</td>
<td>rt</td>
<td>25</td>
<td>0.55</td>
<td>100</td>
<td>53</td>
</tr>
<tr>
<td>9</td>
<td>rt</td>
<td>25</td>
<td>0.55</td>
<td>100</td>
<td>53</td>
</tr>
<tr>
<td>10</td>
<td>rt</td>
<td>25</td>
<td>0.55</td>
<td>100</td>
<td>54</td>
</tr>
<tr>
<td>11</td>
<td>rt</td>
<td>25</td>
<td>0.55</td>
<td>100</td>
<td>56</td>
</tr>
<tr>
<td>12</td>
<td>rt</td>
<td>25</td>
<td>0.55</td>
<td>100</td>
<td>56</td>
</tr>
</tbody>
</table>

The initial polymer, HPM-502, had an apparent molecular weight of \( M_n = 1,390 \) (PDI = 2.39, relative to polystyrene standards). After functionalization to given polymer 3, a moderate increase to \( M_n = 2,700 \) (PDI = 2.73) was seen. The Gaussian appearance of the polymer traces suggest that no metathesis or other redistribution of the silicone occurred. The presence of residual Si-H groups was confirmed by FTIR spectroscopy showing the distinctive Si-H stretch around 2160 cm\(^{-1}\),\(^{63}\) as illustrated in Figure 1. Decreasing the amount of triarylamine 2 used to 0.9 equiv resulted in a similar result: 60% of the hydride functionality was converted (run 2, Table 1).

Continued use of 0.9 equiv of triarylamine 2, but decreasing the concentration of the reaction solution from 25 wt% to 20 and then 15 wt% resulted in 54 and 39 % of the hydride functionality reacting respectively (runs 3 and 4, Table 1). Again by maintaining 0.9 equiv of triarylamine 2 but increasing the temperature to 55 and 80 °C, respectively, and while maintaining a concentration of 25 wt% resulted in ~60% of the hydride functionality reacting (runs 5 and 6, Table 1). The conclusions from these initial experiments are that there is a ceiling above which no further reaction of the hydride occurs. The efficiency ceiling occurs at ~60% conversion and is independent of temperature and the amount of triarylamine 2 present and decreases on decreasing the concentration of the reaction. We concluded that the cause of this observation must be steric in nature whereby the reaction is hindered once a neighbouring hydride, or a series of neighbours, has been substituted with the triarylamine. This occurs even though toluene is a good solvent for the base silicone, the triarylamine and, presumably, a silicone-triarylamine hybrid polymer.

Polymer 3 is a highly viscous oil or glassy solid in appearance even when it contains residual triarylamine. Its physical state makes removal of free triarylamine problematic using
such techniques as selective precipitation, solvent extraction or chromatography on silica or alumina. Therefore, we preferred to develop reaction conditions under which the triarylamine is quantitatively incorporated into the hybrid polymer 3. Given the observed ceiling of 60% conversion of hydride groups we initially tried reacting 0.6 equiv of triarylamine 2 (run 7, Table 1). However, we observed only 82% conversion of the triarylamine. A small reduction to 0.55 equiv of triarylamine resulted in its complete incorporation into the polymer (run 8, Table 1). The only purification that was necessary was removal of the BCF catalyst by treatment of the reaction mixture with a small amount of alumina for a short period of time. Filtration followed by removal of the toluene by rotary evaporation gave the final polymer 3. We found that prolonged stirring of the solution (overnight) in the presence of alumina resulted in the partial hydrolysis of the triarylamine from the silicone polymer, presumably due to the presence of trace amounts of water adsorbed on the alumina surface or present in the toluene. These conditions were subsequently replicated four times with equivalent results (runs 9-12, Table 1).

Having polymer 3 free of residual triarylamine in hand its basic physical properties were determined. The electrochemical properties of 2 and 3 were compared by cyclic voltammetry, the results of which are illustrated in Figure 2. In each case the voltammograms were acquired using the same technique as we have previously published which involves the use of an internal standard of decamethylferrocene. The reversible oxidation of the triarylamine moiety pendant to the silicone copolymer occurs at higher half-wave potential (967 mV) than that of parent triarylamine (807 mV), behavior similar to that previously observed for oligosilicone-functionalized triarylamines.1

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Figure 2: Cyclic voltammogram of triarylamine (2, red) and polymer (3, blue); second cycles only are shown, corrected to the known reference value for decamethylferrocene standard (~0.012 V).

DSC experiments were performed on 2 and 3 whereby the sample was first heated to ~275 °C under inert atmosphere followed by flash freezing to ~75 °C. On second heating a glass transition temperature ($T_g$) was found at ~ 30 °C for 3 and ~ 25 °C for 2 (Figure 3). These are in the $T_g$ range expected for a silicone and the second is in the range shown for structurally related triarylamines. A small melt transition is also observed at ~ 62 °C. While the small melt transition is well below that observed for pure triarylamine 2 (99-101 °C) its presence and the presence of a $T_g$ in the range expected for pure triarylamine would indicate the possibility of significant aggregation of the triarylamine in the solid state.

In order to examine whether aggregation of the triarylamine moieties occurs in polymer 3, UV-Vis absorbance and fluorescence emission spectroscopy was conducted on triarylamine 2 and polymer 3 (Figure 4). In each case the characteristic absorption of the triarylamine was seen (334 nm for triarylamine 2 and 333 nm for polymer 3). Similarly, ordinary fluorescence spectra were observed with Stokes shifts of 73 nm and 71 nm for 2 and 3, respectively, in toluene solution. A fluorescence spectrum obtained on a solid state sample of polymer 3 showed a
nearly identical emission spectrum to the solution sample, albeit with a slightly larger Stokes shift. In an attempt to force aggregation in solution we compared the fluorescence spectrum of polymer 3 in pure toluene to that in a series of solvent mixtures with increasing proportions of hexamethyldisiloxane (HMDS, a non-solvent for the triarylamine). As can be seen in Figure 5 the emission maximum underwent a small hypsochromic shift, but no additional shoulders or structure were seen in the spectrum. The rather ordinary photophysical behavior of polymer 3 both in solution and solid state indicates that if aggregation of the triarylamine does occur (as suggested by the DSC thermogram), it does not result in energy transfer on excitation and emission from an excimer or aggregate.\textsuperscript{65,66} Finally, the hydrolytic stability of 3 was evaluated using FTIR spectroscopy on a thin film of polymer 3 exposed to air at r.t. over a one month period. This was compared to the same treated with acidic standard alumina over a 2d period in solution (conditions mentioned above which results in hydrolysis). The thin film exposed to air showed no change in the FTIR spectrum between 4000-4500 cm\textsuperscript{-1} over time whereas the alumina-treated sample developed an absorbance band at 3546 cm\textsuperscript{-1}, which is attributable to the stretch of an Si-OH bond formed on hydrolysis (Supporting Information, Figure S5). The absence of a 3546 cm\textsuperscript{-1} stretch for the thin film indicates polymer 3 is hydrolytically stable over the period of one month.

2.2 Conclusion

In conclusion, Piers-Rubinsztajn conditions were found to be useful in functionalizing a phenylmethyl-methylhydride silicone copolymer with a triarylamine leading to the formation of a silicone-triarylamine hybrid polymer. The reaction requires very low concentration of the BCF catalyst; workup is clean and straightforward. No redistribution or metathesis of the silicone polymer was observed, and the polymer showed excellent hydrolytic stability in air. We did observe a ceiling whereby only 60% of the hydride functionality present in the silicone polymer could be reacted under these conditions. The hybrid silicone-triarylamine hybrid polymer displayed comparable electronic and optical properties to the parent triarylamine as determined from CV and optical absorption and fluorescence spectroscopy. We can therefore conclude that


Piers-Rubinsztajn conditions are suitable to prepare polymers of this class that have a demonstrated utility in the field where we do not believe the residual hydride functionality would be a problem.

2.3 **Experimental Part**

2.3.1 **Materials and Syntheses**

Toluene was purified using a PureSolv solvent purification system prior to use. Tris(pentafluorophenyl)borane, montmorillonite K10 clay and tetrabutylammonium perchlorate were obtained from Sigma-Aldrich and used without further purification. HPM-502 (methylhydrosiloxane-phenylmethylsiloxane copolymer, 45-50 mol% MeHSiO, hydride-terminated) was purchased from Gelest Inc. (Morrisville, PA, USA) and used without further purification. All other solvents were 99% or higher purity from Caledon Laboratories Ltd. (Brockville, ON, Canada), as was chromatographic silica gel 60 (50-100 µm). Deuterated chloroform (CHCl₃) was purchased from Cambridge Isotopes and used without further purification.

2.3.2 **Characterization Techniques**

Melting points are uncorrected. Triarylamine syntheses were monitored by TLC on SilicaPlate 250 µm thick silica gel with F-254 indicator, using 1:1 (v/v) cyclohexane:toluene as eluent and visualizing using 254 nm and 365 nm UV light. Polymer functionalization was monitored by gel permeation chromatography (GPC) using Waters Styragel® HR 4E THF and Styragel® HR 5W THF columns in series, 5 µm particle size, THF eluent at a flow rate of 1.0 mL/min at 30°C; a photodiode array (254-800 nm) in “MaxPlot” mode was used for detection. Chromatograms were uncorrected by individual compounds’ molar absorptivities. All NMR spectra were collected on a Varian Mercury 400 spectrometer in CDCl₃. Chemical shifts are reported in parts per million referenced relative to tetramethylsilane internal standard. Coupling constants (J) are reported in Hz. High resolution mass spectroscopy was taken with an AB/Sciex QStar mass spectrometer. Samples were introduced with an ESI source in solution (50:50 methanol and water) via an HPLC pump. Cyclic voltammetry (CV) was performed with a Bioanalytical Systems C3 electrochemical cell setup. The working electrode was a 1 mm
platinum disc with a platinum wire used as a counter electrode. The reference electrode was Ag/AgCl saturated salt solution. All electrochemistry was done in ‘Spectro’ grade dichloromethane from Caledon Laboratories with (Bu)$_4$NClO$_4$ as a supporting electrolyte. Decamethylferrocene was added to the solutions as an internal reference. All DSC half wave potentials are reported from the 2$^{nd}$ scan and corrected by the internal reference (-0.012V vs. Ag/AgCl$$_2$).$^{67}$ Fourier transform infrared (FTIR) spectra were recorded on KBr plates using a Perkin Elmer Spectrum 100 spectrometer from 4000-400 cm$^{-1}$. Solution spectroscopy was performed in quartz cuvettes with 1.0 cm path length. Optical absorption measurements were conducted using a Perkin Elmer Lambda 1050 UV/Vis/NIR spectrometer. Fluorescence measurements were conducted using a Perkin Elmer FS55 spectrofluorometer. Polymer films were drop cast onto quartz discs and dried overnight at 80 $^\circ$C under vacuum before fluorescence measurements were taken. Spectra were processed using Spekwin 32 (all types), Perkin Elmer UV Winlab (UV-vis) or FL WinLab (fluorescence) software. Differential scanning calorimetry was performed with a TA Instruments 2920 DSC with a refrigerated cooling system, using Al hermetic pans. Tests were performed under a blanket of nitrogen.

$N$-(3,4-Dimethylphenyl)-4-anisidine (1): Synthesis procedure is similar to that previously reported,$^{64}$ using Buchwald-Hartwig reaction conditions, washing crude product with 1.0M HCl$$_{aq}$ and NaHCO$_3$, and substituting silica gel and montmorillonite K10 clay for alumina and acidic benonite clay. Recrystallization from $n$-heptane yielded white needles (46%). $M_p$ 99-101 $^\circ$C. $^1$H NMR (400MHz, CDCl$_3$) $\delta$ 7.02 (2H, d, $J = 8.9$ Hz), 6.98 (1H, d, $J = 8.2$ Hz), 6.84 (2H, d, $J = 8.9$ Hz), 6.75 (1H, d, $J = 2.2$ Hz), 6.70 (1H, dd, $J_1 = 8.8$Hz, $J_2 = 2.4$ Hz), 5.34 (1H, br s), 3.79 (3H, s), 2.20 (3H, s), 2.19 (3H, s); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 155.3, 143.4, 137.3, 137.3, 130.7, 127.9, 121.5, 118.6, 115.0, 114.6, 55.1, 20.0, 19.0. HRMS (ESI, [M+H]$^+$) calcd for C$_{15}$H$_{18}$NO $m/z$ = 228.1388; found 228.1377.

$N$-(3,4-dimethylphenyl)-N-(4-methoxyphenyl)biphenyl-4-amine (2): Synthesis procedure is similar to that previously reported,$^{68}$ using a bis(dibenzylideneacetone)palladium(0) and tri-$t$-butylphosphine catalyst system, and using silica gel with montmorillonite K10 clay in


purification. Excess 4-bromobiphenyl was distilled off at elevated temperature. Product was recrystallized from n-heptane as fluffy white powder (48%). M_p 134-136 °C. 1H NMR (400MHz, CDCl_3) δ 7.60-7.56 (2H, m), 7.47-7.39 (4H, m), 7.30 (1H, t, J = 7.4 Hz), 7.12 (2H, d, J = 8.8 Hz), 7.05 (3H, d, J = 8.8Hz), 6.95 (1H, d, J = 2.1 Hz), 6.91-6.84 (3H, m), 3.83 (3H, s), 2.25 (3H, s), 2.21 (3H, s); 13C NMR (100 MHz, ) δ 156.0, 147.9, 145.6, 140.8, 137.5, 133.4, 131.1, 130.3, 128.7, 127.5, 127.0, 126.5, 125.5, 121.8, 121.6, 114.7, 55.5, 19.9, 19.1; HRMS (ESI, [M+H]^+) calcd for C_{27}H_{26}NO m/z 380.2014; found 379.2025. UV-Vis (nm) 311.1, 333.2. Fluorescence (nm) 406.2; CV oxidation (mV) 795 vs. Ag/AgCl.

described as follows:

\[ \text{poly[methyl, N-(3,4-dimethylphenyl)-N-(4-biphenyl)-N-(4-phenyloxy)siloxane-co-phenylmethylsiloxane-co-methylhydrosiloxane]} (3):\]  

N-4-anisyl-N-3',4'-xylyl-4-biphenylamine (600 mg, 1.53 mmol), methylhydrosiloxane-phenylmethylsiloxane copolymer (458 mg, 2.78 +/- 0.08 mmol Si-H) and 3.06 mL anhydrous toluene were loaded into a 4-dram vial with stir bar. The vial was heated to the reaction temp if not rt. 115 µL of 0.025 g/mL tris(pentafluorophenyl)borane in anhydrous toluene was then injected, resulting in vigorous bubbling within seconds to <4 min after catalyst addition. Catalyst loading was either 0.25 mol% or 0.50 mol% relative to triarylamine R-O-Ar groups. CAUTION: an exotherm and flammable gas evolution are associated with this reaction, which should be accounted for in larger-scale experiments. Stirring was continued for 20-30 min after bubbling was no longer visible, after which 600 mg basic standard alumina was added, stirred for 20-30 s and the mixture filtered through 0.22 µm PTFE. Overnight stirring with silica or alumina, in ambient conditions or at elevated temp, was found to result in more extensive decomposition and so was avoided. 1H NMR of the purified product showed no detectable toluene after drying overnight at 80°C under vacuum. UV-Vis (nm) 310.7, 331.4. Fluorescence (nm) 402.3 (toluene solution), 406.0 (film); CV oxidation (mV) 891 vs. Ag/AgCl. T_g (°C) 27.8 (2\textsuperscript{nd} heating curve in DSC).
3
Extension of the Application of Piers-Rubinsztajn Conditions to Produce Triarylamine Pendant Dimethylsiloxane and Methylhydrosiloxane Copolymers

This is taken from Gretton, M.J. and Bender, T.P. Manuscript in preparation. Scheme 5 and Table 2 in this chapter were both expanded by Prof. Timothy Bender. All syntheses, materials characterizations and measurements were performed by me.

3.1 Results and Discussion

3.1.1 General reaction methods and conditions

We began by selecting a set of silicones with silane functionality (Si-H) exclusively in the D* position. MD*M (Table 2) represents the smallest (and discrete) oligomer of PMHS and that with which we have previously functionalized a library of arylamines. Four larger, multifunctional oligomers and polymers were chosen for functionalization (Table 2), designated poly-a through poly-d. Poly-a which has low molecular weight with proportionally high silane content was chosen as having physical properties intermediate with the MD*M and the other polymers. Poly-b, a short copolymer similar to poly-a was used only for basic kinetics studies, which are described further in Chapter 4.69 A PDMS-PMHS copolymer and PMHS homopolymer poly-c and poly-d, respectively, complete the set. The basic relevant properties of these silicones are summarized in Table 2 below. Each silicone was reacted under P-R conditions with triarylamine 1 (Scheme 5) as outlined in the Experimental Part below.

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69 “Poly-b” here is the same silicone as “poly-M” in Chapter 4.
Scheme 5. Reaction of model triarylamine (1) with silicone copolymers to produce siliconized arylamines 2, 3 and 4.

To summarize, the silicone was dissolved in anhydrous toluene and after stirring for a short period of time a stock solution of tris(pentafluorophenyl)borane (B(C₆F₅)₃, BCF) in anhydrous toluene was then injected with a micropipettor. The result was typically a vigorous bubbling occurring within seconds to < 1 min after addition accompanied by a noticeable exotherm. The bubbling gas is assumed to be methane and as such its production should be accounted for at larger scale. A variety of catalyst loadings and reagent concentrations were
studied and a 2:1 or higher mole ratio of Si-H groups to triarylamine methoxy (MeOAr) groups was used to try to ensure complete exhaustion of 1 in all cases.

Table 2. Summary of silicones investigated for coupling to triarylamine 1 under P-R conditions.

<table>
<thead>
<tr>
<th>Silicone ID</th>
<th>Chemical Structure</th>
<th>$M_n$ (nominal) [g·mol$^{-1}$]</th>
<th>D–D* ratio$^a$ n:m</th>
<th>% Si-H functionalized after reaction with triarylamine 1.$^b$ Compound designation (% Si-H reacted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD*M</td>
<td><img src="image" alt="MD*M Structure" /></td>
<td>222.51</td>
<td>0:1</td>
<td>3 (100)</td>
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<td>Poly-a</td>
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<td>4:1</td>
<td>4a (50)</td>
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<td><img src="image" alt="Poly-b Structure" /></td>
<td>2100</td>
<td>5:1</td>
<td>4b (N/A)$^c$</td>
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<tr>
<td>Poly-c</td>
<td><img src="image" alt="Poly-c Structure" /></td>
<td>5800</td>
<td>3:1</td>
<td>4c (48)</td>
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<tr>
<td>Poly-d</td>
<td><img src="image" alt="Poly-d Structure" /></td>
<td>2100-2400</td>
<td>0:1</td>
<td>4d (48)</td>
</tr>
</tbody>
</table>

$^a$Dimethylsiloxane-to-methylhydrosiloxane units. $^b$Calculated from GPC integrals based on arylamine functionalization only before finishing with anisole, as in Chapter 2 (ref. 40). $^c$Used for kinetics study only.

3.1.2 Discrete Siliconized Triarylamine 3

The progress of the reaction of triarylamine 1 with MD*M can be conveniently followed using liquid chromatography with UV-Visible detection (via a photodiode array) as the triarylamine chromophore’s photophysical properties, including $\lambda_{max}$, remain similar upon coupling with the silicone (vide supra). While HPLC can be used for the reaction of triarylamine 1 with MD*M, GPC can also be used and so for consistency we chose to use
exclusively GPC. Chromatograms of starting triarylamine 1 and its product on reaction with MD*M, compound 3, are overlaid in Figure S2 in Appendix A showing the purity of the product. The significant shift of the $t_r$ is indicative of a large change in hydrophobicity on reaction with MD*M. Discrete triarylamine 3 was characterized using $^1$H and $^{29}$Si NMR as well as FTIR. Its purity was also confirmed by these methods; Si-H spectroscopic signatures at $\nu_{\text{Si-H}} = 2160$ cm$^{-1}$ in the FTIR spectrum (Figure S6, Appendix B) and around $\delta = 5.3$ ppm in the $^1$H spectrum (Figure S20, Appendix D); and at $\delta \approx -37$ ppm in the $^{29}$Si DEPT NMR spectrum (Figure S21, Appendix D), whether selecting for one-bond or two bond Si-H resonances, corresponding to the D* unit,$^{70}$ were all not present after drying at elevated temperatures to remove excess silicone. A new $^{29}$Si peak in the -60 to -70 ppm range was observed corresponding to the presence of a “T” unit (silicone with three bound oxygens/the formation of the new Si-O bond) of compound 3.

3.1.3 Reaction of Triarylamine 1 with Silane Copolymers and PMHS

In preliminary trials using silane copolymers of $5000 < M_n < 10000$ g·mol$^{-1}$ containing a D-D* ratio of ~5:1 we set the reaction solution concentration at $\approx 15$ wt % solids in toluene which is within the range of 15~25 wt % used in the previous work with methylphenylsiloxane-methylhydrosiloxane (PMPS-co-PMHS) copolymers to produce polymer 2 (Scheme 5).$^{44}$ However, no functionalization of the silicone with triarylamine 1 was detected. We hypothesized that either (1) the Si-H in these silicones were either inaccessible to 1 + BCF in toluene due to the copolymer’s coiling in solution, leaving the silane functionality inaccessible to reaction or (2) the associated molar concentrations of Si-H were too low for probable formation of the termolecular activated complex for reaction.

The $\chi$-parameter values of PDMS ($\chi_{PDMS}$) ranges from 0.445 to 0.82 for 0-100 % polymer (v/v) in toluene at 20°C,$^{71}$ close to the lower limit of 0.5 for full miscibility in the binary system.$^{72}$ This indicated that perhaps the copolymer was coiled in solution and the silane

functionality thus inaccessible to functionalization. Our first strategy to address this issue was to use a mixture of solvents wherein the second solvent would have a favorable $\chi$-parameter. We substituted a fraction of the toluene with 2,2,4-trimethylpentane (TMP), for which $\chi_{PDMS}$ is 0.38-0.44 at rt for 0-100% polymer.\textsuperscript{71} A 2:1 (v/v) toluene:TMP solvent mixture, with the same solids content as above and under the same reaction conditions, did achieve the desired functionalization reaction; however, the starting mixture was heterogeneous due to the insolubility of triarylamine 1 in this solvent system. The reaction did become homogeneous as the reaction proceeded. However, inhomogeneity at any point in the process is undesirable if avoidable.

The second strategy we undertook was to simply conduct the reaction at higher mass concentration, such that the molar concentration of Si-H groups is similar to that which led to the successful functionalization of PMPS-co-PMHS copolymers which was $\geq 0.1$ M. This approach was successful in trials of the same silicone polymers ($5000 < M_n < 10000$ g·mol$^{-1}$ D-D* ratio of ~5:1) and functionalization was observed by GPC but the starting higher-solids content (35~40 wt %) mixture was incompletely dissolved/homogeneous at room temperature. Moreover, we observed macrogelation of the viscous solution occurred during the time required for quantitative conversion.\textsuperscript{73} This gelation was a result of crosslinking (as indicated by the inability to resolubilize the polymer) presumably due to the presence of water and P-R coupling after metathesis. It was therefore decided to attempt the functionalization with lower-molecular weight silane copolymers with larger silane fraction, such that lower solids contents could be used without diluting to excessively low reagent concentrations.

These conditions proved beneficial; gelation of reaction mixture was delayed until after quantitative conversion of/reaction with triarylamine 1 and could be further delayed by neutralizing or removing BCF with neutral alumina. However, to more effectively reduce the extent of unwanted crosslinking at long reaction times, it is necessary to eliminate or ‘finish’ the residual Si-H groups with a monofunctional reagent. One common route to accomplish this is by hydrosilylation of the residual silanes with a simple olefin such as ethylene, propylene, \textit{etc}. In our case, however, the BCF catalyst is still active and can be utilized to effect a further Piers-

\textsuperscript{73} Unpublished results.
Rubinsztajn reaction with a small ether, without introducing any metal species (which are required for hydrosilylation). We chose anisole as a simple and inexpensive reagent to finish the silane groups and lead to a further increase in the phenyl content of the silicone. After the anisole finishing step, crude product solutions are stable over a one-day period in solution and in the presence of BCF, showing only gradual colour formation arising from BCF-arylamine redox equilibrium.\textsuperscript{1a} This colour disappears from the product upon neutralization with triethylamine or treatment with neutral or basic alumina.

We then applied this optimized process to a series of silicone copolymers \textbf{poly-a}, \textbf{poly-c} and \textbf{poly-d} (Table 2). Each silicone has been selected to span a range of \textit{M}_n values and D-D* ratios. Using \textbf{poly-a} as a starting silicone, an intermediate sample’s analytical properties were similar to the discrete siliconized triarylamine 3, with increased broadening of the spectroscopic peaks corresponding to triarylamine moiety in FTIR and \textsuperscript{1}H NMR spectra due to its polymeric nature; this in itself is evidence of successful functionalization of the silicone with the triarylamine. However, the \textit{v}_{\text{Si-H}} stretching band in FTIR, and Si-H peaks in \textsuperscript{1}H and \textsuperscript{29}Si NMR spectra (Figures S22 and S23 in Appendix D, respectively) were still present. Using this information it can be estimated that approximately 50\% of the silane functionality originally present in the starting silicone has been replaced by a triarylamine. This is similar to the behaviour we have previously seen when using methylphenylsiloxane-methylhydrosiloxane (PMPS-co-PMHS) copolymers whereby we achieved a plateau of 60\% functionalization of Si-H groups.\textsuperscript{44} The suggestion is the same as in this case, that a fraction of D* units have been reacted with triarylamine increasing the steric congestion along the polymer backbone such that adjacent D* groups become inaccessible for further reaction of 1. On finishing with anisole the same analytics indicate nearly complete removal of the silane functionality. We can detect small amounts of residual silanes in the FTIR and NMR spectra (Figures S24 to S29); however, given that measurements with each technique were not quantitatively precise, we can only estimate that >90\% of the silanes have been reacted after the entire process.

As with the discrete triarylamine 3, GPC-UV-Visible chromatography can be used to track the progress of the functionalization of \textbf{poly-a}, \textbf{poly-c} and \textbf{poly-d} to give 4a, 4c and 4d respectively. The chromatograms show a clear transition to the molecular weight distribution of the silicone, now containing the UV chromophore (Figure 3). However, a peak at \textit{t}_r \approx 8.0,
showing an optical absorption spectrum within a few nm of 1, appeared in tandem with 4c and 4d and was unchanged after longer ~2 h reaction times or further addition of catalyst. We believe this to be a side product of, for example, BCF-catalyzed metathesis\textsuperscript{31d} of the methoxy group on 1 to a methoxy T site on the silicone, or hydrolysis of pendant triarylamine by adventitious water with BCF acting as a strong Brønsted acid.\textsuperscript{51} Thus, for this class of silicone polymers, there appears to be limitations to the performing of this process in open air conditions which is unlike our previous reported cases of discrete small molecules, oligomers and PMPS-co-PMHS copolymers (2, Scheme 5).\textsuperscript{1,44}

![Normalized absorbance vs. Retention time](image)

**Figure 3. Overlay of GPC traces of triarylamine precursor 1 and functionalized co-oligomer and copolymers 4a/4c/4d. Toluene ($t_r = 9.65$ min) is used as an internal standard.**

While Si-H in these products are <=50 % pendant triarylamine functionalized, a more detailed optimization like that undertaken for the phenylated silicone is likely to increase this to at least the same level of ~60 % based on steric arguments. This is particularly the case for poly-a and poly-c, which appear to have D units interspersed between most D\textsuperscript{*} units in contrast with the bulkier phenylmethylsiloxane units of the phenylated silicone. Thermodynamically, the methylated polymers should become increasingly compatible with arylamines as the functionalization proceeds, a phenomenon observed in the earlier trials with larger copolymers.\textsuperscript{32}
We therefore believe that there is no substantial difference in overall reactivity toward this pendant functionalization between phenylated and methylated silicones.

One potential disadvantage of aryloxy functionalization by P-R chemistry is the question of hydrolytic stability of the product silicones. Although siloxyl bonds are not considered as stable as silyl Si-C bonds, our previous phenylated silicone copolymer showed excellent hydrolytic stability of the aromatic Si-O-C bond in air. We thus anticipate good hydrolytic stability of the finished silicones once BCF is neutralized or removed and, indeed, chromatographic and FTIR data were unchanged over the course of more than 1 month in air after isolation of the products. Furthermore, the FTIR spectra of 4a, 4c and 4d do not show any free Si-OH stretching resonances in the 3600–3800 cm\(^{-1}\) region, just as for 2 previously. Very small peaks corresponding to <0.1 % silanol may be obstructed by water or the presence of hydrogen bonding, but these data indicate that hydrolysis is not a significant problem with the functionalized PDMS and PMHS copolymers.


\footnote{E.D. Lipp, \textit{Appl. Spec.} \textbf{1991}, 45(3).}
As a final note, a series of trials were conducted to monitor the reaction of 1 with poly-b at different starting triarylamine 1 (MeOAr) concentrations for constant 5:1 Si-H: MeOAr mole ratio and catalyst loading (Figure 5). The concentrations selected represent the range of conditions we have found effective for functionalization across all silicones investigated and we were interested to see the effect of concentration on reaction rate. There is clearly a longer induction time and lower overall conversion rate at the lowest concentration relative to the two higher concentrations, and a less-obvious difference between the latter two. Since the 160 mM MeOAr reaction mixture contained over 35% copolymer by mass and was visibly more viscous than the others, it is quite possible that the reaction was under partial microscopic diffusion control in this case. Qualitatively, the kinetics of this reaction in the case of 4a, 4b, 4c and 4d

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Figure 4. FTIR spectra of functionalized methylphenylsiloxane-methylhydridosiloxane copolymer 2 from ref. 40 and functionalized silicone composites 4a, 4c and 4d.

were rapid and followed a logical trend based on molecular weight \((\text{poly-c} > \text{poly-d} \sim \text{poly-b} > \text{poly-a})\) and average steric congestion around Si-H groups of the starting silicone \((\text{poly-a} \sim \text{poly-b} \sim \text{poly-c} > \text{poly-d})\); triarylamine was completely consumed within < 30 mins in all cases.

Figure 5. Influence of reagent concentration on conversion rate and induction time of Piers-Rubinsztajn reaction between triarylamine 1 and short copolymer poly-b to make 4b.

To summarize, Piers-Rubinsztajn conditions have previously been proven effective with a variety of triarylamine substrates, discrete silicones (MM*, MD*M) and phenylated silicones (PMPS-co-PMHS). We have now extended the methodology to a range of methylated silicone polymers. The functionalization with triarylamine 1 proceeded similarly with rapid conversion and triarylamine 1 could be consistently incorporated into at least 46–50% of the D* units of the starting silicones. However, we observed a higher propensity for side reactions leading to gelation when using methylated silicones. To counteract the gelation we developed a ‘finishing’

method involving the use of anisole to react residual Si-H groups thus preventing their ability to participate in crosslinking reactions. Side reactions of up to 3% of triarylamine were observed, limiting the purity of the pendant copolymers when prepared in atmospheric conditions. Nonetheless, the resulting siliconized triarylamines show a range of physical properties that can be easily tuned with the choice of polymer backbone and extent of functionalization, making this a facile and attractive process for the preparation of such materials from inexpensive reagents. These materials are expected to be of significant utility in organic electronic devices.

3.2 Experimental Part

3.2.1 Materials and Syntheses

Unless otherwise specified, solvents and reagents were used as received. Toluene was purified using a PureSolv solvent purification system prior to use. MD*M and the co-oligomers and copolymers of dimethylsiloxane and methylhydrosiloxane designated poly-a, poly-b and poly-c were a gift from Siltech Corp. (Toronto, ON, Canada). MD*M was purified by distillation before use. PMHS (HMS-993) was purchased from Gelest Inc. (Morrisville, PA, USA). Deuterochloroform (CDCl$_3$, 99.8% isotopic purity and benzene-$_6$ (C$_6$D$_6$), 99.5% isotopic purity, were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Tris(pentafluorophenyl)borane (B(C$_6$F$_5$) or BCF) was obtained from Strem Chemicals Inc. (Newburyport, MA, USA) and used without further purification.

3.2.2 Characterization Techniques

Reactions of MM* and MD*M were monitored by high-performance liquid chromatography (HPLC) using a Waters SunFire™ C$_{18}$ column, 3.5µm particle size, acetonitrile eluent at a flow rate of 0.6 mL.min$^{-1}$ at 25°C. A photodiode array (PDA, 190-800 nm) was used for detection and retention times $t_r$ are referenced to toluene. PDA absorption spectra are consistently blue-shifted by 5–6 nm relative to previous measurements on a Perkin Elmer Lambda 1050 UV/Vis/NIR spectrometer. Functionalization of all other silicones were monitored by gel permeation chromatography (GPC) using Waters Styragel® HR 4E THF and Styragel® HR 5W THF columns in series, 5 µm particle size, THF eluent at a flow rate of 1.0 mL/min at 30°C; the same PDA in “MaxPlot” mode was used for detection. Chromatograms were uncorrected by individual compounds’ molar absorptivities. NMR spectra were collected on a Varian Mercury 400 ($^{13}$C
NMR) or Varian VNMRS 400 spectrometer (all others) in CDCl₃ or C₆D₆. ¹H and ¹³C chemical shifts are reported in parts per million referenced relative to (protonated) solvent, and ²⁹Si referencing is done according to the spectrometer frequency. Coupling constants (J) are reported in Hz. Elemental analysis was performed on a Perkin Elmer 2400 Series II CHNS Analyzer. Fourier transform infrared (FTIR) spectra were recorded using KBr plates or as a mull with KBr using a Perkin Elmer Spectrum 100 spectrometer from 4000-450 cm⁻¹.

**N-(3,4-dimethylphenyl)-N-(4-methoxyphenyl)biphenyl-4-amine (1):** Synthesis procedure is as reported in Chapter 2.⁴⁴ Yield 8.39 g (70%). ¹H NMR (400 MHz, C₆D₆) δ 7.55 – 7.40 (m, 4H), 7.26 – 7.21 (m, 4H), 7.22 – 7.20 (m, 1H), 7.16 – 7.13 (m, 1H), 7.13 – 7.09 (m, 2H), 7.04 (dd, J = 8.1, 2.4 Hz, 1H), 6.96 (d, J = 8.1 Hz, 1H), 6.79 – 6.70 (m, 2H), 3.30 (s, 2H), 2.03 (s, 3H), 1.95 (s, 3H); ¹³C NMR (100 MHz, C₆D₆) δ 156.69, 148.63, 146.48, 141.52, 141.43, 137.71, 134.37, 131.24, 130.89, 129.06, 128.13, 127.39, 126.97, 126.83, 126.16, 122.55, 122.51, 115.23, 55.03, 19.82, 19.11, 0.04 (TMS). UV-vis (nm) 326 ± 1. EA calcd for C₂₇H₂₆NO C 85.44 %, H 6.02 %, N 3.99 %; found C 84.72 %, H 6.40 %, N 3.98 %.

**Siliconization procedure for discrete oligomer 3:** N-4-anisyl-N-3',4'-xylyl-4-biphenylamine (300 mg, 0.79 mmol), MD*M (350 mg, 1.6 mmol Si-H) and 1.94 mL anhydrous toluene were loaded into a 50 mL two-necked flask with stir bar. 102 μL of 0.025 g/mL tris(pentafluorophenyl)borane in anhydrous toluene was then injected, resulting in vigorous bubbling within seconds to <1 min after catalyst addition. **CAUTION: an exotherm and flammable gas evolution are associated with this reaction, which should be accounted for in larger-scale experiments.** Catalyst loading ranged from 0.20 mol% to 0.50 mol% relative to triarylamine R-O-Ar groups, and reagent concentrations were typically 0.1~0.2 M. Stirring was continued for 5-15 mins after bubbling was no longer visible, after which a sample was analyzed by HPLC or GPC as appropriate. 15-30 minutes after catalyst addition, 0.17 mL (1.6 mmol) anisole was introduced, resulting in more gas evolution. Once bubbling was no longer apparent, the solution was heated at 50–60 °C for several minutes, typically resulting in additional gas evolution. Once this was no longer visible, the solution was mixed for a further 10 minutes, after which 500 mg basic standard alumina was added, stirred for 20-30 s and the mixture filtered.

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through 0.22 µm PTFE or a fine glass frit, after which the toluene and excess anisole were removed in vacuo at elevated temperature. Yield 0.59 g (74 %). UV-vis (nm) \( \lambda_{\text{max}} \) 326 ± 1. \(^1H\) NMR (400 MHz, C\(_6\)D\(_6\)) \( \delta \) 7.51 – 7.44 (m, 1H), 7.40 (d, \(^2J = 6.6\) Hz, 1H), 7.15 – 7.08 (m, 1H), 7.06 (d, \(^3J = 2.3\) Hz, 1H), 7.03 – 6.96 (m, 3H), 6.92 (d, \(^3J = 8.1\) Hz, 1H), 2.01 (s, 3H), 1.93 (s, 3H), 0.27 (s, 3H), 0.15 (s, 18H).

Siliconization procedure including “finishing” step for comps 4a, 4b, 5.

poly[dimethylsiloxane-co-methyl, N-(3,4-dimethylphenyl)-N-(4-biphenyl)-N-(4-phenyloxy)siloxane-co-methylhydrosiloxane]. 4a: Initial procedure and reagent mole ratios as for 3. CAUTION: an exotherm and flammable gas evolution are associated with this reaction, which should be accounted for in larger-scale experiments. 15-30 minutes after catalyst addition, an amount of anisole 1:1 mole equivalent with the initial Si-H content of the silicone was introduced, resulting in more gas evolution. Once bubbling was no longer apparent, the solution was heated at 50–60 °C for several minutes, typically resulting in additional gas evolution. Once this was no longer visible, the solution was mixed for a further 10 minutes, after which 500 mg basic standard alumina was added, stirred for 20-30 s and the mixture diluted with toluene and filtered through 0.22 µm PTFE or a fine glass frit, after which the toluene and excess anisole were removed in vacuo at elevated temperature. Yield 0.62 g (86 %). UV-Vis (nm) \( \lambda_{\text{max}} \) 330 ± 1. \(^{29}\)Si DEPT NMR (79.4 MHz, C\(_6\)D\(_6\)) \( \delta \) 7.85, 7.31, 7.20, 7.27, 7.20, 6.49, 6.11, 6.99.

4c: Synthetic procedure as for 4a, using silicone poly-c. Yield 0.59 g (81 %). UV-vis (nm) \( \lambda_{\text{max}} \) 330 ± 1. \(^{29}\)Si DEPT NMR (79.4 MHz, C\(_6\)D\(_6\)) \( \delta \) (end groups not observed at this S/N ratio) -20.54, -21.72, -62.02.

4d: Synthetic procedure as for 4a, using silicone poly-d. Yield 0.59 g (74 %). UV-vis (nm) \( \lambda_{\text{max}} \) 329 ± 1. \(^{29}\)Si DEPT NMR (79.4 MHz, C\(_6\)D\(_6\)) \( \delta \) 10.42, -0.48 (TMS), -34.57, -56.35, -56.82, -61.01, -61.72.
4

Controlling the Kinetics of Piers-Rubinsztajn Reaction Across Oligo- and Polysilicones with Triarylamines Having Different Leaving Groups

This is taken from Gretton, M.J.; Kamino, B.A.; Bender, T.P. Manuscript in preparation. The synthesis and purification of triarylamine 1b were performed in consultation with Brett Kamino. All other syntheses and measurements were performed by me.

4.1 Results and Discussion

The basis for this study was to alter the reaction rate of silanes with alkoxy triarylamines under Piers-Rubinsztajn (P-R) conditions which yield siliconized-triarylamines which we refer to as liquid organic semiconductors (LOSs). As outlined in Table 3, we chose to increase the size of the ether group on the triarylamine from one-carbon (methyl, Me, \(-\text{CH}_3\)) to four- and seven-carbon (butyl, Bu, \(-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\) and benzyl, Bn, \(-\text{CH}_2\text{Ph} \) respectively) and study the effect on the reaction rate with two different discrete silanes (MM* and MD*M) and two different polysilicones with silane functionality. By investigating this range of groups we can observe both the magnitude of the change in reaction rate and determine whether the overall reactivity by this pathway is different. In all trials, initial molar concentrations of reagents were kept constant, and a 5:1 mole ratio of Si-H groups to \(\text{ArOR}_3\) (\(\text{R}_3 = \text{leaving group in triarylamines 1a-c} \)) was used. We expect the product’s Si-O-Ar bond to be stable and no further reaction should occur.\(^{35}\)

The progress of reactions, in terms of triarylamine conversion, was followed by either low-molecular weight GPC (reactions involving poly-M or poly-Ph) or HPLC (for MM* and MD*M). In either case eluted species were identified by retention time coupled with absorption spectroscopy via a UV-Visible photodiode array detector. As expected, siliconized triarylamine products were seen at longer retention times than the alkoxy/benzyloxy triarylamine starting materials by HPLC when MM* and MD*M were used and shorter retention times were seen by GPC when poly-M and poly-Ph were used. The percent conversion was calculated as the fraction (area under product peak) ÷ (sum of reactant and product peak areas), using areas of the resolved peaks in the chromatogram (extracted at a wavelength specific for the chromophore – 296 nm or 330 nm), and adjusting reactant and product peak areas for small differences in molar absorptivities. Data
of conversion to product as a function of time (Figures 6 to 9 and S7 to S11 in Appendix C) are labelled according to starting materials, environment and catalyst loading: Me = triarylamine 1a (R₃ = -CH₃); Bu = triarylamine 1b (R₃ = -CH₂CH₂CH₂CH₃); Bn = triarylamine 1c (R₃ = -CH₂Ph); M = MM*; D = MD*M; poly-M = dimethysiloxane-methylhydrosiloxane copolymer; poly-Ph = methylphenylsiloxane-methylhydrosiloxane copolymer; G = glovebox conditions used; and l = one aliquot of 0.5 mol% BCF. For example, Bn_D_G1 was performed in glovebox conditions with an initial charge of 0.5 mol% BCF.

Table 3: Outline of experiments. Precursor triarylamines (1a-c) react with silanes (MM*; MD*M; poly-M; poly-Ph) to yield compounds as indicated (and referred to within the text).

<table>
<thead>
<tr>
<th>Precursor Triarylamine</th>
<th>1a (R₃ = CH₃ = Me)</th>
<th>1b (R₃ = (CH₂)₂CH₃ = Bu)</th>
<th>1c (R₃ = CH₂Ph = Bn)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Silanes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MM*: R₁ = CH₃; R₂ = *-O-Si-CH₃</td>
<td>Me_M</td>
<td>Bu_M</td>
<td>Bn_M</td>
</tr>
<tr>
<td>MD*M: R₁ = R₂ = *-O-Si-CH₃</td>
<td>Me_D</td>
<td>Bu_D</td>
<td>Bn_D</td>
</tr>
<tr>
<td>poly-M: R₁ = R₂ = *-[O-Si]ₙ</td>
<td>Me_poly-M</td>
<td>Bu_poly-M</td>
<td>Bn_poly-M</td>
</tr>
<tr>
<td>poly-Ph: R₁ = R₂ = *-[O-Si]ₙ</td>
<td>Me_poly-Ph</td>
<td>Bu_poly-Ph</td>
<td>Bn_poly-Ph</td>
</tr>
</tbody>
</table>

We began by studying the siliconization of triarylamines 1a-c with MD*M. Figure 6 illustrates the conversion-time profiles compared across leaving groups on the triarylamine (Me,
Bu and Bn). The same plot with a full time scale is included as Figure S7 in Appendix C. This set of data shows two clear points for discussion: firstly, initial and overall conversion rates are lower with larger substituents. In other words and as expected, the reaction rate of 1a (Me) > 1b (Bu) > 1c (Bn). Secondly, although final conversion of 1a (Me) and 1b (Bu) to product are virtually quantitative (in ~1 min and ~120 for Me_D and Bu_D respectively), reaction of the Bn derivative 1c seems to stall at incomplete conversion. Stalling occurs at ~ 60% when 1 or 2 aliquots of catalyst are used (Bn_D_1, Bn_D_2) and at ~92% when 5 aliquots are used (Bn_D_5). Stalling is independent of whether the reaction is carried out in air or the glovebox environment (Bn_D_1.1.1.2 versus Bn_D_G1.1). Near-quantitative (99.8%) conversion can be achieved if a second aliquot of catalyst is added during the reaction conducted in the glovebox environment (Bn_G1.1) but not if it is conducted in air, even after three additional aliquots were added (Bn_D_1.1.1.2).

Figure 6: Kinetics of Piers-Rubinsztajn reaction between MD*M and triarylamines 1a-c (1a = M, 1b = Bu, 1c = Bn).
Next, we substituted the silane MD* for MM* in order to study the effect of moving the reactive silane functionality from a D position to an M position and found nearly identical behavior. A comparison is shown in Figure 7 and a full time scale plot is again provided in Appendix C as Figure S8. The same relative rate relationship applies: 1a (Me) > 1b (Bu) > 1c (Bn), albeit with much higher absolute rates. Reaction of 1a with MM* is practically instantaneous (Me_M) versus ~1 minute for MD*M (Me_D) and reaction of 1b with MM* takes ~3 minutes to reach completion (Bu_M) versus ~120 minutes for the reaction of 1b with MD*M (Bu_D). What is clear from these data is that the Piers-Rubinsztajn reaction of less hindered (terminal) silanes (Si-H) as in MM* is much more rapid as would be expected, although perhaps not expected to this extent. However, we still observed a plateau at ~60% conversion for the reaction of 1c (Bn) with MM* (Bn_M). Quantitative conversion is, however, achieved after a second aliquot of catalyst is added, even several hours later (see Figure S8 in Appendix C).

Figure 7: Kinetics of Piers-Rubinsztajn reaction between M*M (M) or MD*M (D) and triarylamines 1a-c (1a = M, 1b = Bu, 1c = Bn).
MD*M represents a discrete example of the more commonly found polymethylhydrosilicones which contain polymeric D* units. Thus, we next studied the reaction of triarylamines 1a-c with polymethylhydrosilicones we denoted as poly-M and poly-Ph. Poly-M is a copolymer of methylhydrido and dimethyl silicones whereas poly-Ph is a copolymer of methylhydrido and phenylmethyl silicones. A comparison was made between poly-M, poly-Ph and MD*M and the result are displayed in Figure 8 (the same plot with full time scale is included as Figure S9 in Appendix C). Again, the same order of relative rates was observed: 1a (Me) > 1b (Bu) > 1c (Bn) for each of the reactions with poly-M and poly-Ph. However, in each case the rate is somewhat retarded for the polymeric substrates (for example Me_D > Me_P ~ Me_Ph). Again we observed a plateau in conversion of 1c (Bn) to the corresponding polymer only in this case at only ~30%. Oddly, the rate of reaction when the phenylated silicone copolymer (poly-Ph; Bn_Ph in Figure 3) was used was significantly faster with 1c (Bn) than when the methylated copolymer (poly-M; Bn_P in Figure 3) was used. By adding aliquots of catalyst at longer times, conversions of 1c can be pushed higher but still ultimately each reaches a plateau of 58% (for poly-Ph) and 70% (for poly-M) in air. A conversion of 100% can be achieved in the glovebox on addition of a second aliquot of BCF solution after 400 mins (Figure S10 in Appendix C).
Figure 8: Kinetics of Piers-Rubinsztajn reaction of MD\(^\ast\)M (D), short PDMS-PMHS (poly-M) and PMPS-PMHS copolymer (poly-Ph) with triarylamines 1a-c (1a = M, 1b = Bu, 1c = Bn).

Thus, regardless of reaction rate, it seems that the triarylamine 1c (Bn) shows a more limited reactivity than the Me or Bu derivatives. Shortly (<1 min) before conversion of 1c was observed by HPLC, evolution of gas was observed. As toluene is the by product of this reaction it was a puzzling observation. Later additions of catalyst led to less intense but still observable gas evolution for several minutes after addition. At the same time incremental conversion was observed (however never reaching 100%). These combined observations seem to indicate the presence of a side reaction apparent only when triarylamine 1c is used (Bn leaving group, toluene byproduct). The result of the side reaction is loss of reaction presumably from catalyst deactivation.
We chose to further investigate this loss of activity. As a first simple test, the initial catalyst charge was doubled to 1.0 mol% for the reaction of 1c with MM*. As illustrated in Figure 9 (Bn_M_2), this yielded essentially quantitative conversion to siliconized triarylamine. We did note approximately 1 % was transformed to byproducts resolvable by HPLC with UV-visible $\lambda_{\text{max}}$ identical, within uncertainty, to the starting material thus indicating the presence of a trace amount of another triarylamine. These may arise from side reactions such as metathetic exchange of the ether and silane functionalities,\textsuperscript{32b} which would yield triphenylamine and benzyloxy-pentamethyldisiloxane (BnODM). In contrast, starting with MD*M or poly-M and also doubling the initial BCF charge yielded the same 50~60 % plateau in conversion seen above after the second 0.5 mol% aliquot was added (Figure 9 run Bn_D_2). A single, initial charge of 2.5 mol% BCF, however, resulted in much higher conversions: 94 %, 99 % and 99.7 % with MD*M, poly-M and poly-Ph (Figure 4 runs Bn_D_5, Bn_P_5 and Bn_Ph_5) respectively; GPC data showed monomodal distributions of functionalized polymer. The reaction with poly-M, Bn_P_2.3, appeared to stall at $t \approx 25$ mins after addition of 1.0 mol % catalyst, but consumption of arylamine continued from $\approx 70$ mins before reaching a higher plateau; the second segment of this reaction coincided with the appearance of another arylamine-functional polymer seen by GPC (Figure S3 in Appendix A). A second, larger (1.5 mol%) aliquot of catalyst was added at $\approx 190$ mins, and the final conversion, at 67 %, was still lower than with same total catalyst loading delivered all at $t = 0$ for Bn_P_5, although the molecular weight distribution seen by GPC had shifted to higher values (Figure S4 in Appendix A). Data from additional related runs to those in Figure 9 are collected in Figures S10 and S11 in Appendix C.
Based on the data we can then make some preliminary conclusions. First, the reaction rates follow predictable relationships consistent with literature precedent. Universally the reaction rates follow the trend based on the sterics of the leaving group on the triarylamines: 1a (Me) > 1b (Bu) > 1c (Bn). The reaction rates also follow the expected trend with regards to the silane chemical composition and its associated steric bulk: MM* > MD*M > poly-M ~ poly-Ph. While the use of butyl (Bu) as a leaving group does slow the kinetics of the process we still remain concerned that its rate is too fast and it still produces a volatile gas a byproduct – butane. Thus the Bu leaving group only partially mitigates the hazards outlined in the introduction of this paper. The benzyl (Bn) leaving group (of triarylamine 1c), on the other hand, has a conversion.
profile which stalls/plateaus presumably due to deactivation of the catalyst. Not surprisingly, the deactivation can be circumvented by increasing the quantities of BCF added. Since it can be assumed that triarylamines 1a-b show the same mechanistic behaviour regardless of silane reactant, and noting that for 1c the apparent plateau is reached after <1 to >60 mins reaction, we hypothesize that the BCF catalyst initially introduced is deactivated through a chemical pathway present in all reactions (regardless of leaving group) which occurs at a rate proportional to the time required to convert triarylamine 1c to its siliconized counterpart. In other words, the general catalyst deactivation pathway only becomes problematic when the primary (desirable) P-R reaction pathway slows. This deactivation mechanism is not strictly proportional to catalyst turnover or it would manifest itself in all reactions of 1a and 1b with the same 0.5 mol % catalyst loading. The deactivation pathway is present in both the glovebox environment and in the air although more predominant in the air. Lesser incremental conversion with later additions of catalyst may be due to increasing prevalence of side reactions with the reduced concentrations of free ROAr and Si-H moieties.

Besides the Piers-Rubinsztajn reaction, there are at least four known types of reactions that may occur with the system BCF + ROAr + methylhydridosiloxane. Firstly, dismutation of M* units and subsequent oligomerization to M*D,M may occur, but this is slow\textsuperscript{37b} and should not consume the large excess of MM* used before P-R reaction can occur. This may, however, explain the continued evolution of gas in reactions of 1c and MM*, since one of the byproducts of oligomerization is volatile Me\textsubscript{2}SiH\textsubscript{2}. Secondly, M* or D* units could participate in another reaction with BCF, namely, σ-bond metathesis with silane, which generates the more reactive HB(C\textsubscript{6}F\textsubscript{5})\textsubscript{2} (Piers’ borane) \textit{in situ}; the products of side reactions with Piers’ borane cannot activate silane to P-R reaction.\textsuperscript{28a} It was recently shown that R\textsubscript{3}SiD species undergo metathetic H/D exchange with \textit{in situ}-formed HB(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}; R\textsubscript{3}Si(C\textsubscript{6}F\textsubscript{5}) was also observed as a side product.\textsuperscript{78}

A third type of reaction may occur because of the speciation of BCF. Based on \textsuperscript{19}F NMR of the catalyst solution, the water adduct of BCF, [(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}B(OH\textsubscript{2})] is most prevalent (Figure S28 in Appendix D) and this is the species that is introduced at $t = 0$. In this form BCF shows strong Brønsted acidity.\textsuperscript{79} Depending on the amount of water present in solution, further hydrates


[(C_6F_5)_3B(OH_2)]_3H_2O (y = 1, 2) may form. Finally, Stephan and coworkers have found that aromatic substitution reaction at the para C of BCF may occur in the presence of sterically hindered Lewis bases; in the case of bis(mesityl)phosphine, this leads to a zwitterionic phosphonium borate: (C_6F_5)_2BF(C_6F_4)PHAr_2.

In order to probe these side reactions, then, we collected multinuclear NMR data of reaction mixtures with 1c and MM* or MD*M, both in situ and after neutralization using Et_3N. Samples of reactions soon after quantitative conversion of 1a and 1b substrates were also analyzed for comparison purposes. The model systems MM* + BCF, MD*M + BCF, and 1c + BCF were also tested. The detailed analysis of these data (Figures S29 to S52 in Appendix D) is ongoing. One clear result is that for reactions involving 1c, a larger number of fluorinated phenyl groups are seen by ^19F NMR than in analogous reactions with 1b or 1a. Another preliminary conclusion therefore arises: the Bn triarylamine derivative introduces additional interactions with BCF that lead to a further deactivation pathway. This pathway appears proportional to turnover as evidenced by the early plateau of conversion after <5 mins reaction in “Bn_M” and “Bn_P_1.1.3” (Figures 7 and 8).

4.3 Experimental Part

4.3.1 General and analytical methods

All siloxanes were used as received unless otherwise specified. Toluene was purified using a PureSolv solvent purification system (Innovative Technology, Amesbury, MA, USA) prior to use. 1,1,1,3,5,5,5-heptamethyltrisiloxane, MD*M and a M_p = 2100 g.mol^{-1}, equiv mass = 420 g.mol^{-1} trimethylsilyl-terminated dimethylsiloxane-hydromethylsiloxane copolymer were graciously donated by Siltech Inc. (Toronto, ON, Canada). MD*M was purified by bulb-to-bulb distillation before use. Pentamethyldisiloxane and dimethyldimethylsiloxane were purchased from Gelest Inc. (Morrisville, PA, USA). Triarylamine 1a was kindly supplied by Xerox Research Centre of Canada (Mississauga, ON, Canada).

\(^1\text{H}\) and \(^{13}\text{C}\) spectra were recorded using either a 400 MHz Bruker Avance® or 400MHz Varian VNMRS® or Mercury® 400 spectrometer and referenced to protonated \(\text{C}_6\text{D}_6\) (7.15 or 128.06 ppm relative to TMS) where present, with a first set of scans used to minimize spectral width before rescanning. All other spectra were absolutely referenced to the proton spectra; \(\text{C}_6\text{F}_6\) internal standard for \(^{19}\text{F}\) NMR samples appeared at -162.85 ppm. \(^{29}\text{Si}, \, ^{11}\text{B}\) and some \(^{19}\text{F}\) NMR spectra were collected on the VNMRS® with x2093 tuned and broadband probe. Selected reaction samples using the benzyloxy-triarylamine were further analyzed by \(^{19}\text{F}\) direct-detect and gradient COSY experiments on the VNMRS® and an Agilent 500 MHz DirectDrive 2 spectrometer. An exponential apodization function was applied before Fourier transform of all \(^{29}\text{Si}\) FIDs, with line-broadening (lb) coefficients based on FWHM of the narrowest peak without lb. Chemical shifts are reported in ppm.

Mass spectra were collected on either a Waters TOF-MS high-resolution mass spectrometer with EI source and accurate mass determination or an AB/Sciex QStar mass spectrometer with an ESI source in positive ion mode and accurate mass capabilities. Melting points were measured using a Stuart® SMP3 melting point apparatus and are uncorrected. Molar extinction coefficients for arylamines were determined by standard methods. For siloxanes-arylamine composites, the Piers-Rubinsztajn coupling was first run to completion (monitored by GPC, UV-visible PDA detection). The product solution was then analyzed by the same spectroscopic methods, and the molar absorptivity of the product back-calculated using the known composition of the starting solution.

All reactions were performed in oven-dried glassware under dry Ar unless otherwise specified. TLC was performed on SiliaPlate 250um thick silica gel with F-254 indicator, using 1:1 (v/v) cyclohexane:toluene as eluent and visualizing using 254 nm and 365 nm UV light. Reactions involving dimethylsiloxane-methylhydrosiloxane or phenylmethylsiloxane-methylhydrosiloxane copolymers were monitored by gel permeation chromatography (GPC) using Waters Styragel® HR 4E THF and Styragel® HR 5W THF columns in series, 5 μm particle size, THF eluent at a flow rate of 1.0 mL.min\(^{-1}\) at 30°C; all other reactions were monitored by high-performance liquid chromatography (HPLC) using a Waters SunFire™ C\(_{18}\) column, 3.5μm particle size, acetonitrile eluent at a flow rate of 0.6 mL.min\(^{-1}\) at 25°C. A photodiode array (254-800 nm) was used for detection. Chromatograms were extracted at \(\lambda = \)
295 nm (all diphenylamine-derived chromophores) or 330 nm (the asymmetric triarylamine 3c) using Waters Empower 2.0 software, and are corrected by individual compounds’ molar absorptivities at the same wavelength. The hydromethylsiloxane-phenylmethylsiloxane copolymer was found to have a negligible absorptivity at these wavelengths before functionalization with triarylamine.

4.3.2 Preparation of alkoxy or aryloxy functional diarylamine precursors

1-Bromo-4-butoxybenzene: 10.10 g (57 mmol) 4-bromophenol, 16.27 g (107 mmol) K$_2$CO$_3$ and 118mL DMF were added to a 250mL round bottom flask fitted with a stir bar and condenser. A rubber septum was fitted and the flask was filled with Ar, followed by addition of 10.70 g (114 mmol) 1-chlorobutane. The heterogeneous mixture was heated at reflux while mixing vigourously. After 22 h the mixture was cooled and filtered, then purified by bulb-to-bulb distillation to afford a colourless oil (10.93 g, 83%), which was used without further purification. $^1$H and $^{13}$C NMR spectral data matched those from the literature.$^{82}$

1-Bromo-4-benzyloxybenzene: Synthesis and purification as for 1-bromo-4-butoxybenzene. 7.51 g (43.4 mmol) 4-bromophenol, 5.15 mL (43.3 mmol) benzyl bromide were reacted using 8.26 g (59.1 mmol) potassium carbonate in 106 mL DMF. The distilled product solidified to an off-white solid (9.40 g, 82%), which was used in the next synthetic step without further purification. A portion was further purified by recrystallization from 20:1 (v/v) hexanes:ethyl acetate to give white needles (Mp 63-66°C, $^1$H and $^{13}$C NMR spectral data matching those from the literature).$^{83}$

N-(3,4-Dimethylphenyl)-4-anisidine: Synthesis and purification as for N,N-bis(4-methoxyphenyl)amine. 4.67 g (38.6 mmol) 3,4-dimethylaniline and 6.01 g (32.1 mmol) 4-bromoanisole were reacted using 4.63 g (48.2 mmol) sodium t-butoxide, 94 mg (0.16 mmol) Pd(dba)$_2$ and 2.69 mL 0.01 g/mL toluene solution of P(t-Bu)$_3$ (0.13 mmol) in 24 mL toluene. Recrystallized product was white needles (46%).Mp 99-101°C. $^1$H NMR (400MHz, CDCl$_3$) $\delta$ 7.02 (2H, d, $J = 8.9$ Hz), 6.98 (1H, d, $J = 8.2$ Hz), 6.84 (2H, d, $J = 8.9$ Hz), 6.75 (1H, d, $J = 2.2$ Hz), 6.70 (1H, dd, $J_2 = 8.8$Hz, $J_3 = 2.4$ Hz), 5.34 (1H, br s), 3.79 (3H, s), 2.20 (3H, s), 2.19 (3H,

$^{82}$ Denmark, S.E.; Smith, R.C.; Tymonko; S.A. Tetrahedron, 2007, 63(26), 5730–5738.
\[ ^{13}C \text{NMR (100 MHz, CDCl}_3 \] \[ \delta = 155.3, 143.4, 137.3, 137.3, 130.7, 127.9, 121.5, 118.6, 115.0, 114.6, 55.1, 20.0, 19.0. \] 
HRMS (ESI, [M+H]\(^+\)) calcd for C\(_{15}\)H\(_{18}\)NO \(m/z = 228.1388\); found 228.1377.

4.3.3 Preparation of monofunctional alkoxytriarylamines and aryloxytriarylamines.

4-Methoxytriphenylamine (1a): Light orange solid, used as received. Mp 106-108°C. \(^1\)H and \(^{13}\)C NMR spectral data matched those from the literature.\(^{84}\) HRMS (ESI, [M+H]\(^+\)) calcd for C\(_{19}\)H\(_{18}\)NO \(m/z = 276.1388\); found 276.1388.

\(N\)-(4-Butoxyphenyl)-diphenylamine (1b): 5.00 g (21.8 mmol) 4-bromo-1-butoxybenzene, 2.96 g (17.5 mmol) diphenylamine, 1.47 g (26.2 mmol) sodium \(t\)-butoxide and 1.0 x \(10^{-1}\) g (0.18 mmol) Pd(dba)\(_2\) were loaded into a 100 mL round bottom flask equipped with stir bar and condenser with gas inlet and mineral oil bubbler. A rubber septum was added and the vessel was purged with dry Ar for 10 minutes, after which 11.0 mL anhydrous toluene was introduced by syringe. After mixing thoroughly, the contents were deoxygenated by three pump-Ar refill cycles. 1.9 mL toluene containing 0.01 g/mL P(\(t\)-Bu)\(_3\) (0.09 mmol) was added by syringe. The mixture was heated to reflux for 1.5 h. The mixture was cooled and filtered through a plug of silica gel, which was further washed with 1:1 (v/v) cyclohexane:toluene. The solvents were removed \textit{in vacuo}, after which the excess 4-bromo-1-butoxybenzene was distilled off at elevated temperature. Crude product was precipitated in methanol, filtered and washed with cold methanol, then filtered through a plug of montmorillonite K10 clay using toluene as eluent. The eluate was dried \textit{in vacuo} and recrystallized from methanol to give white needles (4.06 g, 73%). Mp 59-61°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) and \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) data matched those from the literature.\(^{85}\) HRMS (ESI, [M+H]\(^+\)) calcd for C\(_{25}\)H\(_{22}\)NO \(m/z = 318.1858\); found 318.1858.

\(N\)-(4-Benzylxyphenyl)-diphenylamine (1c): Synthesis and purification as for \(N\)-(4-butoxyphenyl)-diphenylamine, with precipitation of crude product first from 2-propanol, giving beige-white powder, which was then recrystallized from \(n\)-heptane or ethyl acetate to give white powder (4.93 g, 79%). Mp 119-121°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.46-7.36 (4H, m), 7.35-\)

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7.30 (1H, m), 7.23-7.18 (4H, m), 7.09-7.01 (6H, m), 6.97-6.89 (4H, m). $^{13}$C NMR (100 MHz, C$_6$D$_6$) δ 155.9, 148.8, 141.6, 137.7, 129.5, 128.7, 127.7, 127.6, 123.5, 122.3, 116.1, 70.3. HRMS (ESI, [M+H]$^+$) calcd for C$_{25}$H$_{22}$NO m/z 352.1701; found 352.1715.

4.3.4 Typical procedure for Piers-Rubinsztajn reaction of methoxy-, butoxy- and benzyloxy-functional triarylamines with oligosiloxanes and silicone copolymers.

(N,N-diphenyl-N-(4-phenyloxy))-1,1,3,3,3-trimethyldisiloxane, (N,N-diphenyl-N-(4-phenyloxy))-methylbis(trimethylsiloxy)silane, poly[methyl(N,N-diphenyl-N-(4-phenyloxy))siloxane-co-dimethylsiloxane-co-methylhydrosiloxane] products of reactions in Table 3: Triarylamine, hydrido-functional silicone and toluene solvent were loaded into a 4-dram vial equipped with stir bar. After stirring to dissolve, a 0.5 mol% aliquot of tris(pentafluorophenyl)borane was injected as a 0.01 g/mL solution in toluene at time = 0. Samples were withdrawn and diluted immediately for HPLC or GPC analysis; multiple injections showed no further reaction after dilution. In some experiments, additional aliquots of the same catalyst solution were added at recorded times.
5
General Conclusions and Recommendations

5.1 Conclusions

A summary of conclusions from the previous chapters is given below. My exposition of the recommendation numbered (1) stems from an idea elaborated by Prof. Timothy Bender and that of number (2) stems from an idea elaborated by Brett Kamino.

Firstly, phenylated silicones are amenable to functionalization with triarylamines. The reaction proceeds rapidly, on a time scale of minutes. It also runs cleanly with minimal side reactions, such as the metathesis that has been observed by other researchers with some sets of reagents and experimental conditions. The side-chain functionalization, which forms an Si-O-C\text{Ar} bond in place of the C-O-C\text{Ar} bond of the starting triarylamine, has minimal effect on photophysical properties (absorption, fluorescence), and fundamental electrochemistry is the same albeit with a small shift in oxidation potential consistent with earlier published work from our group.\textsuperscript{1} Thermal behaviour of both silicone and triarylamine are seen; a $T_g$ characteristic of the free triarylamine is observed, but the product takes the physical appearance of a viscous liquid or glassy solid polysilicone.

Phenylation is not, however, a prerequisite for formation of triarylamine pendant silicone copolymers; methylhydrosiloxane-dimethylsiloxane copolymers are similarly amenable to functionalization. Regardless of methyl or phenyl substituents on the siloxane backbone, if the effective concentrations of reacting groups – Si-H, ROAr and BCF – are high enough, the chemistry will proceed. Thus, experimental conditions were found for which a range of siliconized products can be made, from discrete small molecules to a copolymer of $>10$ kDa molecular weight. Functionalized oligomers and phenylated copolymers can be isolated in high (99–99.9%) purity. In all polysilicones investigated, there exists an upper limit in terms of fraction of reactive Si-H groups (for triarylamines). These groups are present in the final polymers but are not expected to influence optoelectronic performance.

In the less sterically hindered PDMS and PMHS copolymers, metathesis and related reactions with water and unfunctionalized Si-H moieties are more problematic under ambient
conditions. If left unaddressed, at longer times this leads to extensive crosslinking and the formation of an insoluble gel. A method was devised to avoid this outcome: further "finishing" of most remaining Si-H groups using P-R conditions and the addition of a smaller substrate, anisole. This step enables the soluble side-chain polymers to be isolated. However, the aforementioned side reactions lead to up to a few percent of unreactive free triarylamine impurities in multifunctional higher-molecular weight products. Such impurities could be detrimental in view of device applications if the electronic structure of the layer is affected (formation of electronic traps, etc.).

The syntheses just described all use a methoxylated triarylamine as a precursor, which reacts very vigourously with the release of a flammable gas - methane. This may introduce safety issues on scale-up, and is a clear drawback if uniform film formation is desired, e.g. in organic electronic device fabrication. This issue applies to all Lewis acid-catalyzed silylation reactions. Therefore, triarylamine derivatives with bulkier leaving groups which produce less volatile byproducts were investigated. As predicted by the literature background for this chemistry, which involves a concerted $S_N2$-Si reaction step and shows third-order kinetics for the related hydrosilylation, increasing steric bulk around either the Si-H or alkyl/aryl ether groups significantly retards the kinetics. Full conversion was observed in <1 minute in the fastest case, to >60 minutes with a butoxylated triarylamine and PDMS-PMHS copolymer. However, the benzyloxy derivative of the same triarylamine stalls at incomplete conversion with the same catalyst loading. This derivative would be attractive since the dehydrocarbonation simply generates more toluene (the solvent) and not a gaseous byproduct. With this substrate, though, additional catalyst loading is required to achieve complete conversion. It appears that the catalytic system with BCF is gradually deactivated through a side reaction which decomposes the BCF. The side reaction is present in all cases of P-R reaction with triarylamine ethers, but the deactivation becomes most prevalent (problematic) when the kinetics of the intended reaction are slowed. In addition, the benzyloxy triarylamine substrate may give rise to further side reactions that are proportional to catalyst turnover.
5.2 Recommendations/Future Work

In the previous chapters, limited mention was given to materials optimization of the siliconized triarylamine products. It is clear, based on the functionalized polymers 3 from Chapter 2 and 4 from Chapter 3, that the percolation threshold of charge-transporting arylamine content mentioned in section 1.5 can be met by more than one candidate. For example, the side-chain PMHS polymer 4d contains approximately 61 wt. % triarylamine assuming 10 % unreacted D* groups. It is thus feasible to tune the physical properties of these composites based on the ratio of D, D*, and pendant arylamine and phenoxy-substituted groups. The latter aromatic side groups will contribute to raising viscosity and \( T_g \) and of the composite, whereas the methylated silicone units have very low glass transition temperatures: \(-138 \, ^\circ C\), \(-123 \, ^\circ C\) and \(-33 \, ^\circ C\) for PMHS, PDMS and PMPS, respectively.\(^{86}\) An optimization of these materials should therefore be undertaken to find compositions which can achieve the required balance of physical and optoelectronic performance.

The research described in this thesis has advanced the application of P-R chemistry to prepare functional materials with properties that are promising in view of utilization in organic electronic devices. In order to further develop these or similar siliconization procedures to produce, more specifically, a soft hole transport layer in a working device, efforts should also be made to address the limitations encountered with catalysis using BCF. It seems the following two avenues are open to further exploration:

(1) Continue to utilize BCF as catalyst, but change the substrate.

New arylamine substrates can be sought that do not give off volatile byproducts but have rapid kinetics. This is important from the perspective of upscaling the reaction, particularly due to its exothermic nature and concomitant temperature rise of the reaction mixture in the fastest <10 minute reactions. In fact, it would be preferable to use an arylamine substrate with no leaving group at all, which might therefore participate in fewer side reactions leading to catalyst deactivation. An idea to achieve this, which originated in the group, is to use cyclic rather than linear ethers of arylamines. There is already at least an example in the literature of successful siliconization of a bicyclic benzofuran by P-R chemistry.\(^{40}\)

(2) Use a catalyst that is more stable than BCF under the desired reaction conditions.

A few criteria for such an “ideal catalyst” can be defined. Firstly, it should be metal-free as BCF is, for reasons outlined in Ch.1. Secondly, it should have kinetics that are either inherently slower than BCF for triarylamine functionalization, or a catalytic mechanism that enables straightforward tuning of the reaction rate based on steric and/or leaving group as in Ch. 4. Finally, and in contrast with BCF, its activity should be relatively stable over a ~1 h time span; that is, it should not be prone to side reactions that render the catalyst inactive within the length of time required for quantitative functionalization with arylamine and formation of a film to be incorporated in an optoelectronic device. A few inexpensive candidates for such a catalyst exist: other halogenated arylboranes with a different balance of Lewis acidity and electrophilicity,\textsuperscript{87, 28b} and halides of other group 13 elements besides the fluorides.\textsuperscript{87b, 88}

The kinetics investigations described in Chapter 4 do not include a detailed kinetic analysis of actual reaction rates and concentrations (activities) of the active species, similar to that performed by Chojnowski and coworkers.\textsuperscript{31d} Based on the known mechanism of the Piers-Rubinsztajn reaction, metathesis and related side reactions also catalyzed by BCF, such an analysis can be undertaken. This may be helpful in clarifying the extent to which side reactions influence the intended arylamine conversion with catalyst turnover, or the relative rates of dehydrocarbonative condensation and metathesis, depending on arylamine substrate.

As a result of my thesis and its conclusions, these lines of investigation are either planned or already being pursued by other researchers in my group.


Appendix A: Analytical chromatograms

Figure S1: Overlaid gel permeation chromatogram of HPM-502 silicone copolymer (left) and compound 3 after purification (right). Molecular weight distributions (relative to narrow polystyrene standards): HPM-502 (g.mol\(^{-1}\)) Mn = 1390, Mw = 3320, Mp = 2310, PDI = 2.39; comp. 3 (g.mol\(^{-1}\)) Mn = 2700, Mw = 7390, Mp = 3580, PDI = 2.73. (Chapter 2)
Figure S2: HPLC traces of precursor triarylamine 1, crude and purified product 3 with catalyst and excess starting material removed. (Chapter 3)

Figure S3: Reaction “Bn_P_2.3” using 3c + 6, 1.0 mol% BCF, additional 1.5 mol% BCF added at t = 190 mins. Sample at 189 mins. (Chapter 4)
Figure S4: Reaction “Bn_P_2.3” using 3c + 6, 1.0 mol% BCF, additional 1.5 mol% BCF added at t = 190 mins. Sample after t = 1 d. (Chapter 4)
Figure S5: FTIR spectrum of film of compound 3 after one month exposure to air (grey trace) and 2 d stirring with acidic Al$_2$O$_3$ (black trace). (Chapter 2)
Figure S6: FTIR spectra of precursor arylamine 1 and functionalized silicones 3 and 4a. (Chapter 3)
Appendix 3: Conversion-time plots from kinetics studies

Figure S7: Kinetics of Piers-Rubinsztajn reaction between MD*M and different alkoxyarylamine/aryloxyarylamine substrates. (Chapter 4)
Figure S8: Kinetics of Piers-Rubinsztajn reaction between M*M or MD*M and different alkoxyarylamine/aryloxyarylamine substrates. (Chapter 4)
Figure S9: Kinetics of Piers-Rubinsztajn reaction of internal Si-H functionality in MD*M, short PDMS-PMHS copolymer (poly_M) and PMPS-PMHS copolymer (poly_P). (Chapter 4)
Figure S10: Kinetics of Piers-Rubinsztajn reaction of Bn triarylamine derivative 1c with silicones at different catalyst loadings.
(Chapter 4)
Figure S11: Expansion of Figure S10 for clarity: $t = 0$ to 300 min. (Chapter 4)
Appendix 4: NMR spectra

Figure S12: $^1$H NMR spectrum (400 MHz, CDCl$_3$) of $N$-(3,4-dimethylphenyl)-4-anisidine (1). (Chapter 2)

Figure S13: $^{13}$C NMR spectrum of $N$-(3,4-dimethylphenyl)-4-anisidine (1). (Chapter 2)
Figure S14: $^1\text{H}$ NMR spectrum (400 MHz, CDCl$_3$) of N-(3,4-dimethylphenyl)-N-(4-methoxyphenyl)-[4,4’-biphenyl]-1-amine (2). (Chapter 2)

Figure S15: $^{13}\text{C}$ NMR spectrum (400 MHz, CDCl$_3$) of N-(3,4-dimethylphenyl)-N-(4-methoxyphenyl)-[4,4’-biphenyl]-1-amine (2). (Chapter 2)
Figure S16: $^1$H NMR spectrum (400 MHz, CDCl$_3$) of polymer 3. (Chapter 2)

Figure S17: $^{13}$C NMR spectrum (400 MHz, CDCl$_3$) of polymer 3. (Chapter 2)
Figure S18. $^1$H NMR spectrum of starting material 1. (Chapter 3)

Figure S19. $^{13}$C NMR spectrum of starting material 1. (Chapter 3)
Figure S20. $^1$H NMR spectrum of discrete siliconized triarylamine 3. (Chapter 3)

Figure S21. $^{29}$Si DEPT NMR spectrum of discrete siliconized triarylamine 3. (Chapter 3)
Figure S22. $^1$H NMR spectrum of pendant oligomer 4a. (Chapter 3)

Figure S23. $^{29}$Si DEPT NMR spectrum of pendant oligomer 4a. (Chapter 3)
Figure S24. $^1$H NMR spectrum of pendant polymer 4c. (Chapter 3)

Figure S25. $^{29}$Si DEPT NMR spectrum of pendant polymer 4c. (Chapter 3)
Figure S26. $^1$H NMR spectrum of pendant polymer 4d. (Chapter 3)

Figure S27. $^{29}$Si DEPT NMR spectrum of pendant polymer 4d. (Chapter 3)
Figure S28: $^{19}$F NMR spectrum of BCF mixed with Et$_3$N in C$_6$D$_6$, with C$_6$F$_6$ added as internal standard. (Chapter 4)

Figure S29: $^1$H NMR spectrum of reaction “Me_M” neutralized with Et$_3$N <10 min after addition of catalyst. (Chapter 4)
Figure S30: $^{29}$Si DEPT NMR spectrum of reaction “Me_M” neutralized with Et$_3$N <10 min after addition of catalyst. (Chapter 4)

Figure S31: $^{11}$B NMR spectrum of reaction “Me_M” neutralized with Et$_3$N <10 min after addition of catalyst. (Chapter 4)
Figure S32: $^{19}$F NMR spectrum of reaction “Me_M” neutralized with Et$_3$N <10 min after addition of catalyst. (Chapter 4)
Figure S33: $^1$H NMR spectrum of reaction “Me_M” neutralized with Et$_3$N ~200 min after addition of catalyst. (Chapter 4)
Figure S34 (left): $^{29}$Si DEPT NMR spectrum of reaction “Me_M” neutralized with Et$_3$N ~200 min after addition of catalyst. (Chapter 4)

Figure S35 (right): $^{11}$B NMR spectrum of reaction “Me_M” neutralized with Et$_3$N ~200 min after addition of catalyst. (Chapter 4)
Figure S36: $^{19}$F NMR spectrum of reaction “Me_M” neutralized with Et$_3$N ~200 min after addition of catalyst. (Chapter 4)
Figure S37 (left): $^{29}$Si NMR spectrum of reaction “Bu_D” neutralized with Et$_3$N after quantitative conversion of 1b. (Chapter 4)

Figure S38 (right): $^{11}$B NMR spectrum of reaction “Bu_D” neutralized with Et$_3$N after quantitative conversion of 1b. (Chapter 4)
Figure S39: $^{19}$F NMR spectrum of reaction “Bu_D” neutralized with Et$_3$N after quantitative conversion of 1b. (Chapter 4)
Figure S40 (left): $^{29}$Si DEPT NMR spectrum of reaction “Bn_D” neutralized with Et$_3$N at t≈200 mins. (Chapter 4)

Figure S41 (right): $^{11}$B NMR spectrum of reaction “Bn_M” neutralized with Et$_3$N after partial conversion (<20 mins). (Chapter 4)
Figure S42: $^{19}$F NMR spectrum of reaction “Bn_M” neutralized with Et$_3$N after partial conversion (<20 mins). (Chapter 4)
Figure S43: $^{11}$B NMR spectrum of reaction “Bn_D” neutralized with Et$_3$N at $t \approx 200$ mins. (Chapter 4)
Figure S44: $^{19}$F NMR spectrum of reaction “Bn_D” neutralized with Et$_3$N at t≈200 mins. (Chapter 4)
Figure S45: $^{19}$F NMR spectrum of BCF mixed with MM* in C$_6$D$_6$. (Chapter 4)
Figure S46: $^{19}$F COSY spectrum of BCF mixed with MM$^*$ in C$_6$D$_6$. (Chapter 4)
Figure S47: $^{19}$F NMR spectrum of BCF mixed with MD*M in $\text{C}_6\text{D}_6$. (Chapter 4)
Figure S48: $^{19}$F COSY spectrum of BCF mixed with MD*M in C$_6$D$_6$. (Chapter 4)
Figure S49: $^{19}$F NMR spectrum of reaction “Bn_M_2” neutralized with Et$_3$N after quantitative conversion. (Chapter 4)
Figure S50: $^{19}$F COSY spectrum of reaction “Bn_M_2” neutralized with Et$_3$N after quantitative conversion. (Chapter 4)
Figure S51: $^{19}$F NMR spectrum of reaction “Bn_D_2” neutralized with Et$_3$N after quantitative conversion. (Chapter 4)
Figure S52: $^{19}$F COSY spectrum of reaction “Bn_D_2” neutralized with Et$_3$N after quantitative conversion. (Chapter 4)