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Extension of the Application of Piers-Rubinsztajn Conditions to Produce Triarylamine Pendant Dimethylsiloxane Copolymers

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Summary: In this paper we show how the strong organic Lewis acid catalyst, tris(pentafluorophenyl)borane ($B(C_6F_5)$ or BCF), can be used to facilitate the functionalization of simple polymeric silicones with a triarylamine yielding a novel class of charge transporting materials. The reaction conditions we refer to as Piers-Rubinsztajn Conditions and we have previously shown such conditions to be suitable when using phenylated silicones as precursors. In this work we found they also work successfully for a silicone oligomer as well as cocopolymers of polymethylhydridosiloxane (PMHS) and polydimethylsiloxane (PDMS) and a PMHS homopolymer, all of which are highly abundent and available in industrial quanitities. The resulting material was either a waxy solid, viscous oil or a glass. An additional "finishing" step with anisole using the same chemistry was found necessary to prevent gelation of the copolymer and homopolymer of PMHS. Even after finishing a small fraction (<5%) of Si-H groups remained in the silicones. This nonetheless provides a rapid and mild method to synthesize functional silicones and tune their physical properties, using commonly available starting materials.

Keywords: catalysis; charge; finishing; free; functional; functionalization; group; materials; metal; polymers; silicones; transport

Introduction

Triarylamines are a class of well-characterized high-performing organic charge transporting materials.[1] Triarylamines are generally crystalline solids at room temperature with solubility in common organic solvents such as aromatics, ethers, esters and halogenated alkanes.[2a,b] The application of triarylamines in novel organic electronic device configurations would be enhanced by facile, orthogonal processability from solution[3] coupled with maintaining or improving the charge carrier mobility of these materials. Our group has been active in the development of *soft* triarylamines which we define as those which are either liquids, waxes or glassy solids at room temperature or moderate temperatures (<60 °C). The synthetic methodology we have developed to obtain soft triarylamines involves their siliconization. We have successfully applied our methodology to simple triarylamines (Figure 1),[2a] two-nitrogen centered tetraaryl-biphenyldiamines, tetraaryl-phenylenediamines and carbazoles (Figure 2).[2b] We have recently shown that siliconized triarylamines can be considered as traditional organic semiconductors as they follow the traditional theory describing charge carrier transport. We have therefore dubbed this class of materials LOSs – liquid organic semiconductors.[4] The mechanical flexibility of LOSs may enable new innovations in solid-state organic lighting,[5] organic light emitting diodes[6] and organic

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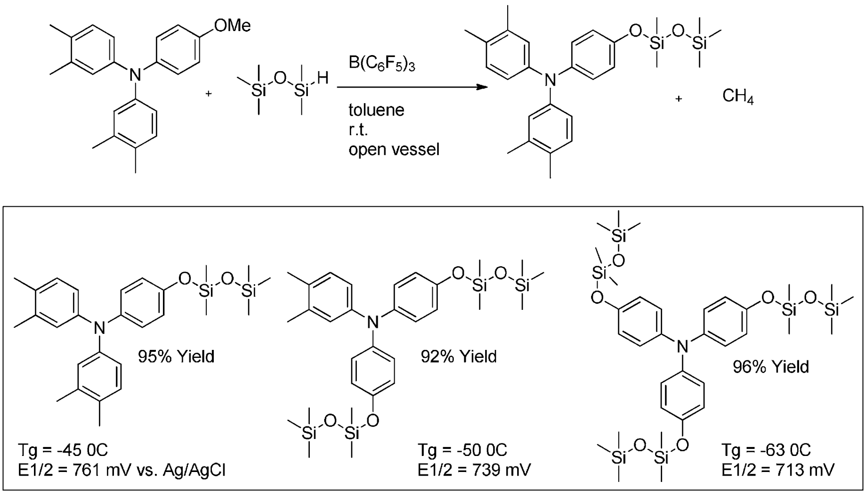

Figure 1.
Example triarylamines which react under Piers-Rubinsztajn (P-R) conditions to yield siliconized triarylamines. Representative physical properties are given for reference.[2a]

photovoltaics:[7] for example, by forming the material into morphologies for more efficient photon collection or outcoupling.[7b] Siliconized charge transport materials may show improved interfacial properties in a multilayer device.[8] For example, Archambeau *et al* have shown that introducing an ultrathin surface wetting layer improved the fill factor and, thus, efficiency of an organic solar cell;[9] Li and Marks have demonstrated an organic light-emitting diode (OLED) that showed analogous performance enhancement with a siliconized hole injection/transport interlayer;[10] finally, siliconized charge transport materials showing liquid-crystalline self-assembly have the potential for higher charge carrier mobilities which is known for other liquid-crystalline materials.[11]

There are several examples of polysiloxanes (polysilicones) which have been pendant functionalized with triarylamines or

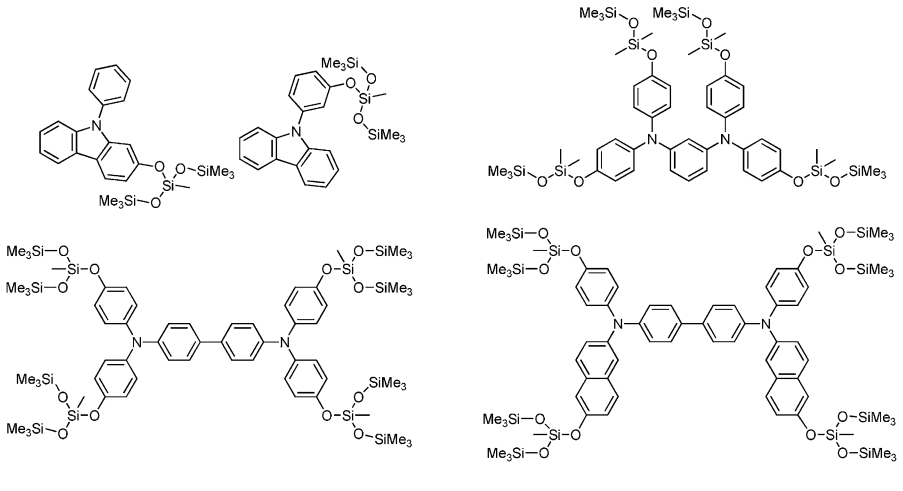

Figure 2.
Example siliconized triarylamines made using Piers-Rubinsztajn (P-R) conditions.

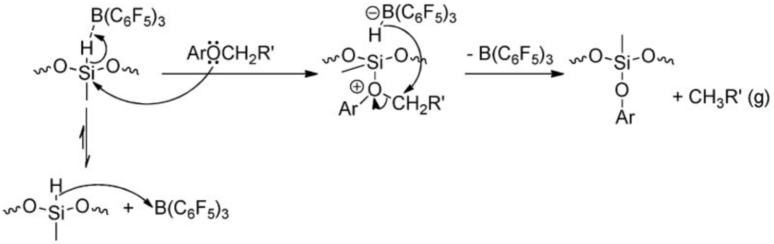

Figure 3.
General mechanism of the Piers-Rubinsztajn reaction for a generic aryl ether. In our case Ar = triarylamine and R′ = H.

their derivatives.[12] Both pre-[13] and post-polymerization synthetic strategies have been utilized, with silane coupling methods such as hydrosilylation being most common in the latter case, catalyzed by hexachloroplatinate(IV) hydrate, Karstedt's catalyst or other Pt or Ru complexes.[14] Researchers have grafted moieties with complementary optoelectronic behaviour to the same silicone polymer backbone;[15] silicone polymers with a sequence of HOMO energy levels enabled higher-efficiency deep blue-emitting OLEDs.[16] Such pendant polymers are advantageous with respect to film forming and facile solution processing,[15,17] but if transition metal catalyst (such as Pt, Pd, Ru) remains in the polymer during device fabrication, it may provide sites for optoelectronic processes detrimental to performance such as charge trapping.[18] We are therefore interested in alternative, straightforward and versatile chemical pathways to prepare arylamine side-chain polymers as a material which has significant interest and demonstrated potential.[15a,c,5b,19]

Mentioned above, the synthetic methodology our group has developed utilizes the bulky and strong Lewis acid $B(C_6F_5)_3$ (hereinafter 'BCF').[20] BCF has the uncommon ability to activate Si–H bonds to nucleophilic attack at silicon by ethers,[21] alcohols,[22] enones,[23] acyl groups,[24] imines and even some alkenes[25] and thiols,[26] enabling hydrosilylation as well as dehydrogenative or dehydrocarbonative condensation reactions. This process has been termed the Piers-Rubinsztajn (hereinafter P-R) reaction[22a,24b,21a,26,27] or P-R conditions, for cases involving alkyl and aryl ethers, alcohols and silanols or alkoxysilanes. The accepted mechanism for reaction is illustrated in Figure 3 for a "D*"[§] unit of methylhydrosiloxane. Although triarylamines are Lewis basic and can interact with BCF,[28] we have found triarylamines have sufficient steric hindrance and are sufficiently weak as Lewis bases that they do not fully quench BCF's activity and therefore triarylamine ethers can be used to functionalize siloxanes using mild conditions as in Figure 1.[2a]

For example, we have also shown that a methylphenylsiloxane-methylhydrosiloxane (PMPS-co-PMHS) copolymer achieved 60% functionalization of Si–H groups at room temperature in ~10 minutes under P-R conditions using a model triarylamine (1, Scheme 1).[2c] The resulting polymer showed good hydrolytic stability of the Si–O–triarylamine bond as a thin film and retained the photophysical and electrochemical properties of the triarylamine. This polymer is analogous to the ones outlined above obtained by hydrosilylation[14] and can be expected to have similar utility, which we are currently working to prove. A phenylated silicone was initially chosen for functionalization with the triarylamine due

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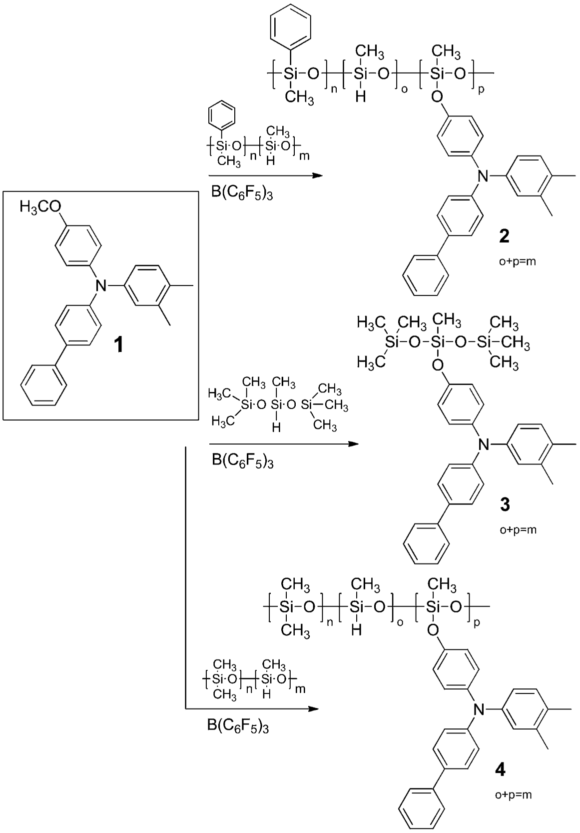
[§] Throughout this manuscript we will use the nomenclature established by General Electric with '*' indicating Si-H functionality, and 'M', 'D' and 'T' denoting a silicon atom with one, two and three oxygen atoms attached, respectively; D* then has the formula $[RSi(H)O_{2/2}]$ in a polysilicone.



Scheme 1.
Reaction of model triarylamine (1) with silicone copolymers to produce siliconized arylamines 2,[2c] 3 and 4.

to its expected better compatibility and, therefore, reactivity with the model triarylamine 1. However, silicones with simultaneous phenyl and silane functionality are very rare whereas silicones with simultaneous methyl and silane functionality are not. We wish to report the extension of our work to the investigation of the reaction of the model triarylamine 1 with dimethylsiloxane-methylhydrosiloxane copolymers (PDMS-co-PMHS) under P-R conditions. This work furthers the scope and limitations of P-R conditions when concerned with triarylamines and silicones; in particular, how the conditions and chemistry utilized for the pre-phenylated silicone might or might not translate to exclusively methylated silicones. We have examined a silicone oligomer, copolymers of PMHS and PDMS and a PMHS homopolymer. The range of silicones we used are inclusive of a broad range of per-chain Si-H functionality and PDMS content. We also describe an additional ‘‘finishing’’ step using anisole which follows directly after the functionalization with triarylamine 1, which we have proven to be necessary when exclusively methylated silicones are used under ambient conditions to prevent crosslinking leading to gelation.

Experimental Part

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. 1,1,1,3,5,5,5-heptamethyldisiloxane (MD*M) and the copolymers of dimethylsiloxane and methylhydrosiloxane designated **poly-a**, **poly-b** and **poly-d** were a gift from Siltech Corporation (Toronto, ON, Canada). MD*M was purified by distillation before use. PMHS (HMS-993, **poly-c**) was purchased from Gelest Inc. (Morrisville, PA, USA). Deuterochloroform ($CDCl_3$).99.8% isotopic purity and benzene-d_6 (C_6D_6), 99.5% isotopic purity, were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Tris(pentafluorophenyl)borane ($B(C_6F_5)$ or BCF) was obtained from Strem Chemicals Inc. (Newburyport, MA, USA) and used without further purification.

Characterization Techniques

Functionalization of all silicones 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) with THF as the eluent at a flow rate of 1.0 mL/min and at a constant temperature of 30 °C. A photodiode array (PDA, 190–800 nm) was used for detection and retention times t_r are referenced to toluene. Two-dimensional chromatograms were extracted using the "MaxPlot" mode. Chromatograms were uncorrected by individual compounds' molar absorptivities. THF and the starting polysiloxanes are isorefractive and are presumed to be not detectable by the PDA. The addition of the triarylamine groups to the polysiloxanes made them detectable and enabled the GPC-UV-Vis analysis of functionalized polymer. 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. NMR spectra were collected on a Varian Mercury 400 (^{13}C NMR) or Varian VNMRS 400 spectrometer (all others) in $CDCl_3$ or C_6D_6. ^1H and ^{13}C chemical shifts are reported in parts per million referenced relative to (protonated) solvent, and ^{29}Si referencing is done according to the spectrometer frequency.[29] Coupling constants (J) are reported in Hz. Elemental analysis was performed on a Perkin Elmer 2400 Series II CHNS Analyzer. Fourier transform infrared (FT-IR) spectra were recorded using KBr plates or as a mull with KBr using a Perkin Elmer Spectrum 100 spectrometer from 450–4000 cm^{-1}.

N-(3,4-dimethylphenyl)-*N*-(4-methoxyphenyl)biphenyl-4-amine (1)

Synthesis procedure is as previously reported.[2c] Yield 8.39 g (70%). ^1H NMR (400 MHz, C_6D_6) 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); ^{13}C NMR (100 MHz, C_6D_6) 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 $C_{27}H_{26}NO$ 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. 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 through

0.22 μm PTFE or a fine glass frit and alumina solids washed twice more with toluene, after which the toluene and excess anisole and MD*M were removed *in vacuo* at elevated temperature. Yield 0.59 g (74%). UV-vis (nm) λ_{max} 326 ± 1. ^{1}H NMR (400 MHz, C_6D_6) δ 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, $^2J = 8.1$ Hz, 1H), 2.01 (s, 3H), 1.93 (s, 3H), 0.27 (s, 3H), 0.15 (s, 18H). ^{29}Si NMR (79.4 MHz, C_6D_6) δ 9.39, -0.47 (TMS), -60.22.

Siliconization Procedure Including "Finishing" Step for 4a. 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. 15–30 minutes after catalyst addition, an amount of anisole in 1:1 mole ratio with initial silicone Si–H functionality 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) λ_{max} 330 ± 1. ^{29}Si DEPT NMR (79.4 MHz, C_6D_6) δ 7.85, 7.31, −20.27, −20.64, −21.44, −61.18, −61.99.

4b

Synthetic procedure as for **4a**, using silicone **poly-b**. Yield 0.59 g (81%). UV-vis (nm) λ_{max} 330 ± 1. ^{29}Si DEPT NMR (79.4 MHz, C_6D_6) δ (end groups not observed at this S/N ratio) −20.54, −21.72, −62.02.

4c

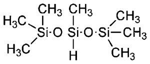
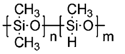
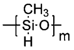
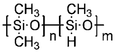
Synthetic procedure as for **4a**, using silicone **poly-c**. Yield 0.59 g (74%). UV-vis (nm) λ_{max} 329 ± 1. ^{29}Si DEPT NMR (79.4 MHz, C_6D_6) δ 10.42, −0.48 (TMS), −34.57, −56.35, −56.82, −61.01, −61.72.

Results and Discussion

General Reaction Methods and Conditions

We began by selecting a set of silicones with silane functionality (Si-H; denoted by a '*' accompanying either and M or D which in themselves denote, respectively, a silicone atom with either one or two oxygen atoms attached)§ exclusively in the D* position. MD*M (Table 1) represents the smallest (and discrete) oligomer of PMHS and that with which we have previously functionalized a library of arylamines.[2b] Four larger, multifunctional oligomers and polymers were chosen for functionalization (Table 1), designated poly-a through poly-c. 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-d, a short copolymer similar to poly-a, was used only for basic kinetics studies.[30] A PDMS-PMHS copolymer and PMHS homopolymer poly-b and poly-c, respectively, complete the set. The basic relevant properties of these silicones are summarized in Table 1 below. Each silicone was reacted under P-R conditions with triarylamine **1** (Scheme 1) as outlined in the preceding experimental section. To summarize, the silicone and triarylamine were dissolved in anhydrous

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

Silicone ID	Chemical Structure	M_n (nominal) [g · mol^{-1}]	D – D* ratio[a] *n:m*	% Si–H functionalized after reaction with triarylamine 1.[b] Compound designation (% Si–H reacted)
MD * M		222.51	0:1	**3** (100)
Poly-a	 $\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n\left[\overset{CH_3}{\underset{H}{Si}}-O\right]_m$	1100	4:1	**4a** (50)
Poly-b		5800	3:1	**4b** (48)
Poly-c	 $-\left[\overset{CH_3}{\underset{H}{Si}}-O\right]_m$	2100–2400	0:1	**4c** (48)
Poly-d	 $\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n\left[\overset{CH_3}{\underset{H}{Si}}-O\right]_m$	2100	5:1	**4d** (N/A)[c]

[a]Dimethylsiloxane-to-methylhydrosiloxane units. [b]Calculated from GPC integration based on triarylamine functionalization only before finishing with anisole, as in ref. 2c. [c]Used for kinetics study only.

toluene and a stock solution of tris(pentafluorophenyl)borane ($B(C_6F_5)_3$, BCF) in anhydrous toluene was then injected with a micropipette. The result was typically a vigorous bubbling which occurred within seconds to < 1 min after addition. Bubbling was also 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 and appropriate safety measures should be taken.* A variety of catalyst loadings and reagent concentrations were studied and a 2:1 or higher mol ratio of Si-H groups to triarylamine methoxy (MeOAr) groups was used to try and ensure complete exhaustion of 1 in all cases.

Discrete Siliconized Triarylamine 3

Triarylamine **1** which contains a methoxy group was synthesized as we have previously described.[2c] ^{1}H and ^{13}C NMR spectra of triarylamine **1** are given for reference in Figures S1 and S2 respectively. The progress of the reaction of triarylamine **1** with MD*M can be conveniently followed using liquid chromatography with UV-Visible detection (via a photo diode array) as the triarylamine chromophore's photophysical properties, including λ_{max}, remain similar upon coupling with the silicone (*vide supra*).[2c] 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. On complete reaction and workup, discrete triarylamine **3** was characterized using ^{1}H and ^{29}Si NMR as well as FT-IR and its identity and purity was confirmed; Si-H spectroscopic signatures at a $\nu_{Si\text{-}H} = 2160$ cm^{-1} in the FT-IR spectrum (Figure 4); around $\delta = 5.3$ ppm in the ^{1}H spectrum (Figure S3) and at $\delta \approx -37$ ppm in the ^{29}Si DEPT NMR spectrum (Figure S4, selected for one-bond Si–H resonances) corresponding to MD*M[31] were not present after drying at elevated temperatures to remove excess MD*M. A new ^{29}Si peak in the $\delta = -60$ to -70 ppm range was observed corresponding to the presence of the new "T" unit (silicone with

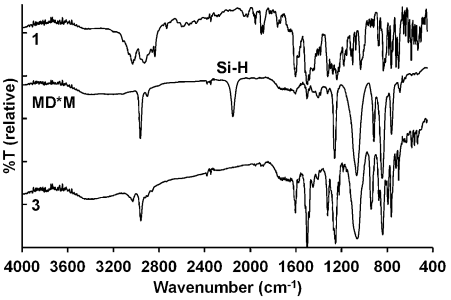


Figure 4.
FT-IR spectrum of triarylamine **1**, MD*M and discrete triarylamine **3**.

three bound oxygens/the formation of the new Si–O bond) of compound **3**.

Reaction of Triarylamine 1 with Silane Copolymers and PMHS

In preliminary trials using silane copolymers of $5000 < M_n < 10000\ g \cdot mol^{-1}$ containing a D-D* ratio of ∼5:1 we set the reaction solution concentration at ≈15 wt % solids in toluene. This concentration 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 1).[2c] However, no functionalization of the silicone with triarylamine 1 was detected. We initially hypothesized that the Si–H in these silicones were inaccessible to 1 + BCF in toluene due to either (1) the copolymer was coiled in solution leaving the silane functionality inaccessible to reaction or (2) that the associated molar concentrations of Si–H were too low for probable formation of the termolecular activated complex for reaction.

Considering (1), The χ-parameter values of PDMS (χ_{PDMS}) range from 0.445 to 0.82 for 0–100% polymer (v/v) in toluene at 20°C, [32] which is close to the lower limit of 0.5 for a fully miscible binary system.[33] This indicated to us that perhaps the copolymer was coiled in solution and the silane functionality thus inaccessible to functionalization. Our strategy to address this issue was to use a mixture of solvents whereby the second solvent would have a more favorable χ-parameter. We substituted a fraction of the toluene with 2,2,4-trimethylpentane (TMP), for which χ_{PDMS} is 0.38–0.44 at rt for 0–100% polymer (v/v).[32] 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 a 2:1 (v/v) toluene:TMP mixture. The reaction did become homogeneous as the reaction proceeded. However, inhomogeneity at any point in the process is undesirable if avoidable.

Considering (2), we undertook simply to 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 >≈0.1 M. This approach was successful in trials of the same silicone polymers ($5000 < M_n < 10000\ g \cdot mol^{-1}$ D-D* ratio of ∼5:1). The starting higher-solids content reaction mixture (35∼40 wt %) was not completely dissolved/homogeneous at room temperature but nonetheless functionalization of the silicone with the triarylamine was observed by GPC. Moreover, we observed macrogelation of the viscous solution occurred during the time required for quantitative conversion. 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.

This selection of silicone and the associated conditions proved successful; 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, we found that is it favourable to eliminate or ‘finish’ the residual Si–H groups with a monofunctional reagent. Oxidation of Si-H,[34a] hydrolysis under acidic or basic conditions,[34b] as well as metal- or BCF-catalyzed dehydrogenative silylation,[34a,35,22,36] are all known and would be potential useful for removing residual Si–H groups. However, each would likely require different reaction conditions. Since the BCF catalyst is still active and can effect a further Piers-Rubinsztajn reaction, though, we chose anisole (phenyl methyl ether) as a simple and inexpensive reagent to finish the silane groups *via* in one-pot (one reaction vessel) without changes in experimental conditions. Incorporation of anisole has the additional benefit of increasing the phenyl content of the final 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.[2a,b] This colour disappears from the product upon neutralization with triethylamine or treatment with neutral or basic alumina.

We then applied this optimal process to a series of silicone copolymers **poly-a**, **poly-b** and **poly-c** (Table 1). Each silicone has been selected to span a range of M_n values and D-D* ratios. Using **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 FT-IR and ^{1}H NMR spectra due to its polymeric nature, which unto itself is evidence of successful functionalization of the silicone with the triarylamine. ^{29}Si NMR data further showed new "T" units in the spectra of all siliconized triarylamines corresponding to the Si–O bonds formed (Figures S6, S8 and S10). However, the ν_{Si-H} stretching band in FT-IR, and Si–H peaks in ^{1}H and ^{29}Si NMR spectra were still present. Using the ^{1}H NMR spectrum it could be verified that approximately 50% of the silane functionality originally present in the starting silicone was replaced with a triarylamine. Previously, when using the same triarylamine and methylphenylsiloxane-methylhydrosiloxane (PMPS-co-PMHS) copolymers, we achieved a maximum of 60% functionalization of Si–H groups.[2c] While Si–H in **4a** to **4c** 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. The reasoning is the same in this case, that a fraction of D* units have been reacted with the triarylamine increasing the steric congestion along the polymer backbone such that adjacent D* groups become inaccessible for further reaction with **1**.

On finishing with anisole, the same analytics indicate nearly complete removal of the silane functionality. No residual silane was detected using ^{1}H or ^{29}Si NMR (Figure S5 and S6 respectively). We could detect small amounts of residual silanes in the FT-IR spectrum. However, given this spectroscopic technique (Figure 5) is not fully quantitative we can only estimate, by comparison before and after functionalization with the areas of characteristic silicone peaks (e.g. Si–O–Si stretching vibrations in the range $\nu = 1020{\sim}1100\ cm^{-1}$)[37,34] that >95% of the silanes have been reacted after the entire process. A similar conclusion can be drawn for **4b** (^{1}H and ^{29}Si NMR spectra are given in Figures S7-S8). As for **4c**, which used PMHS homopolymer as its starting material, residual silane can be seen in the FT-IR spectrum (Figure 5; $\nu = 2190\ cm^{-1}$), the ^{1}H (Figure S9; $\delta = 5.04$ ppm) and ^{29}Si NMR (Figure S10; $\delta = -34.56$ ppm). Using this information we can estimate that even after finishing with anisole ~20% of residual silane is still present in **4c**.

As with the discrete product **3**, GPC-UV-Visible chromatography can be used to track the progress of the functionalization of poly-a, poly-b and poly-c to give **4a**, **4b** and **4c** respectively (Figure 6). The chro-

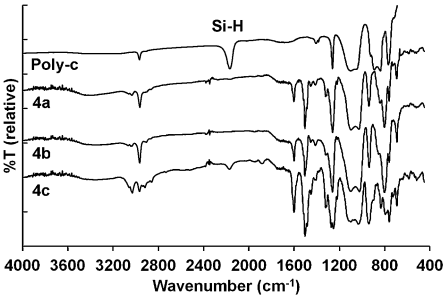


Figure 5.
FT-IR spectra of PMHS (**Poly-c**) and triarylamine functionalized silicones **4a**, **4b** and **4c**.

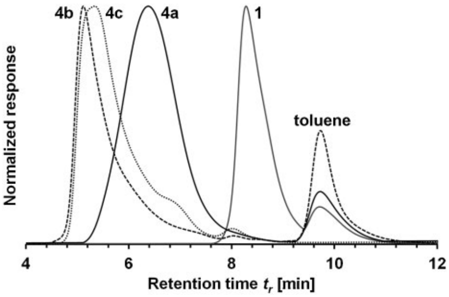


Figure 6.
Overlay of normalized GPC traces of triarylamine precursor **1** and functionalized silicones **4a/4b/4c** (toluene ($t_r \approx 9.65$ min) is used as an internal standard).

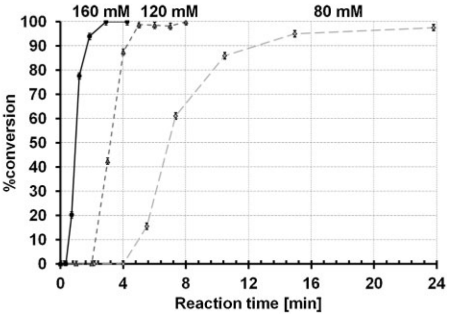


Figure 7.
Influence of reagent concentration on conversion rate and induction time of Piers-Rubinsztajn reaction between triaryl**amine 1** and short copolymer **poly-d** to make **4d**.

matograms show a clear transition to the molecular weight distribution of the silicone, now containing the UV chromophore. However, a peak at $t_r \approx 8.0$, showing optical absorption maxima within a few nm of **1**, appeared in tandem with **4b** and **4c** 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 of the methoxy group on **1** to a methoxy T site on the silicone,[27c] or hydrolysis of pendant triarylamine by adventitious water with BCF acting as a strong Brønsted acid.[38] 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 1).[2]

We now address the question of hydrolytic stability of the new aryloxy functionalization present in the silicone. Although Si–O–C 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/ambient conditions.[2c] We thus anticipate good hydrolytic stability of the finished silicones once BCF is neutralized or removed. Indeed, chromatographic and FT-IR data were unchanged over the course of more than 1 month in air after isolation of the products. Furthermore, the FT-IR spectra of **4a**, **4b** and **4c** do not show any free Si–O–H present which would be indicated by the unique O–H stretching vibrations which would be present in the 3600–3800 cm^{-1} region of the FT-IR spectrum.[39] We should note however that it is known that very small FT-IR peaks corresponding to <0.1% silanol can be obstructed by water or the presence of hydrogen bonding,[40] but again we do not observe native water either. Thus we can conclude that hydrolysis is not a significant problem with the functionalized PDMS and PMHS copolymers.

As a final note, a series of trials were conducted to monitor the reaction of **1** with **poly-d** at different starting MeOAr concentrations for constant 5:1 Si–H: MeOAr mole ratio and catalyst loading (Figure 7). 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.[41] Qualitatively, the kinetics of this reaction in the case of **4a**, **4b**, **4c** and **4d** were rapid and followed a trend based on molecular weight (**poly-b** $>$ **poly-c** $\sim$ **poly-d** $>$ **poly-a**) and average steric congestion around Si-H groups of the starting silicone (**poly-a** $\sim$ **poly-b** $\sim$ **poly-d** $>$ **poly-c**). However, regardless of conditions or silicone used triarylamine **1** was completely consumed within $<$ 30 mins in all cases.

Conclusion

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 the triarylamine 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. A triarylamine-containing side product was 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.

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