Spring 5-14-2022

Preparation and Evaluation of Methytrifluoropropyl-Containing Vinyl-Functionalized Terpolysiloxanes for “All-in-One” Pastes for Additive Manufacturing

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Recommended Citation

Satterfield, Hunter, "Preparation and Evaluation of Methytrifluoropropyl-Containing Vinyl-Functionalized Terpolysiloxanes for “All-in-One” Pastes for Additive Manufacturing" (2022). *Electronic Theses & Dissertations*. 395.
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PREPARATION AND EVALUATION OF METHYTRIFLUOROPROPYL-CONTAINING VINYL-FUNTIONALIZED TERPOLYSILOXANES FOR "*ALL-IN-ONE*" PASTES FOR ADDITIVE MANUFACTURING

A Thesis Submitted to the Graduate School
in Partial Fulfillment of the Requirements
for the Degree of
Master of Science

Hunter James Satterfield

Pittsburg State University

Pittsburg, Kansas

May 2022

PREPARATION AND EVALUATION OF METHYTRIFLUOROPROPYL-CONTAINING VINYL-FUNTIONALIZED TERPOLYSILOXANES FOR “*ALL-IN-ONE*” PASTES FOR ADDITIVE MANUFACTURING

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ACKNOWLEDGMENTS

I would like to express my deepest appreciation to my advisor Dr. Petar Dvornic for his unrelenting support and supervision and tutelage during my time here at Pittsburg State University in both my undergraduate and graduate degrees. I am extremely thankful for his constant support so that I could become the best I could be. Dr. Dvornic is an extremely passionate person when it comes to polymer chemistry especially silicones and I am grateful that I was able to learn through him during my time at Pitt State. I would also like to express my appreciation to Mr. James Beach who has helped mentor me to learn and grow my knowledge throughout my graduate program.

I would like to also thank Dr. Bobby Winters, Chemistry Department Chair, for giving me the opportunity to be a Graduate Research Assistant here at Pitt State University. I would also like to thank every PSU staff member that I have had the privilege of working with during my time at PSU both for my undergraduate and graduate degrees.

This thesis was realized as a part of the ongoing program funded by Honeywell Federal Manufacturing and Technologies, LLC (contract numbers in 2021 and 2022 0000446223 and N000419162) and I gratefully acknowledge this financial support. In addition, I would also like to thank our extremely collegiate and constructive collaborators from Honeywell, including Mr. Steven Patterson, Ms. Jeannie Salah and Dr. Jamie Messman, without whose help and support this work would have never been completed. Special thanks go to Mr. Nathan Pickering for providing NMR spectra and analyses of the polymer samples described in this work.

I would also like to express my love and gratitude to my family and friends especially my lovely fiancée Hope Lindner for supporting me throughout my undergraduate and graduate degrees. Without their support I wouldn’t be here today, and they have all done amazing jobs assuring that I am working hard but also teaching me to take breaks and enjoy the little things.

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An Abstract of the Thesis by
Hunter Satterfield

In this work, the effects of the degree of polymerization (DP) and incorporation (mol %) of methytrifluoropropylsiloxy (MeTfpS) repeat units into vinyl-functionalized terpolysiloxanes in crosslinked elastomers from *“All-in-One”* pastes (A/1Ps) for additive manufacturing were investigated. It was found that the DP and mol % of MeTfpS-containing repeat units do not contribute to the rheological properties of non-crosslinkable pastes, which can be mostly attributed to the thixotropic additive and both the type and relative amount of filler added. Crosslinkable A-1/Ps with higher DP polymers exhibited faster curing (crosslinking) while the mol % of MeTfpS had little to no effect on the curing times. A/1Ps underwent a year-long shelf-life stability study indicating only a slight loss in storage modulus for pastes using MeTfpS-containing terpolymers with targeted DPs of 160 and 240 after six months. The crosslinked elastomers exhibited strain-induced crystallization (via DMA) only in elastomer samples containing 5 mol % of MeTfpS and with a DP of 240 or higher in the temperature range of -80 to -30 °C, characteristic for pure polydimethylsiloxane (PDMS) melting transition.

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CHAPTER I

INTRODUCTION

1.1 Additive Manufacturing

Additive manufacturing (AM), more commonly known as 3D-printing, is the process of making three-dimensional (3D) solid objects of any shape and size from a digital model by adding material(s) under continuous computer control. AM is considered distinct from traditional machining techniques because, rather than removing material through cutting drilling, AM places successive layers of material on top of one another to build different solid shapes. This method of manufacturing is precise and creative, allowing for little to no waste of material and energy during the manufacturing process, and is becoming more and more economical. AM technology is currently used for both prototyping and distributed manufacturing with applications in automotive, aerospace, and engineering to list a few.[1] AM is changing the way products are designed, produced, and serviced, and is already using a wide range of materials from polymers (namely plastics), metals, and biomaterials to “print” layer after layer of material into the designated shape.[1]

There are currently two main types of technologies utilizing 3D printers widely used in AM of polymers; fused deposition modeling (FDM) and stereolithography (SLA). FDM is currently the most widely used type of 3D printing for consumers. It works by melting a filament of thermoplastic material, such as acrylonitrile-butadiene-styrene (ABS) or poly(lactic acid) (PLA) in an “extruder”, ejecting the melt through a heated nozzle, and applying the melted plastic layer by layer to create the shape of the printed object. SLA uses a thermoset liquid resin (acrylates, epoxy, etc.) rather than a hard thermoplastic filament. The printing platform is lifted from the liquid resin while a laser draws the shape on the base of the platform. The resin is cured by the laser using a process called photopolymerization. SLA printing is widely used to make prototypes due to its high-accuracy and smoother finish over the FDM but requires more post-processing of parts and is more costly to run.[2]

Direct Ink Writing (DIW) is a new and rapidly developing method for 3D printing. It uses an extrusion-based technique like FDM, but rather than a solid thermoplastic, a molten liquid “ink” is dispensed out of extruder nozzle forming a preset pattern layer-by-layer to acquire the part. DIW is becoming more widely used due to its ability to print in the meso- and micro-scales accurately.[3]

1.2 The problem of printing rubber parts

Presently, a rather fast development in printing technologies and printer construction is nowhere near matched with the utilization of printing ink materials. In the polymer field, these materials are mostly limited thermoplastics, such as ABS, PLA, nylon, polycarbonate, polyester copolymers, and polyether imide, which have conveniently high melting temperatures that enable easy melting in extruder and fast solidification into desired shapes of printed objects when extruded into room temperature environments.[4,5] However, the problem arises with elastomers which, if semicrystalline, by their nature have melting temperatures way below ambient temperature so that other ways of their transition from solid to liquid and back is needed.[5]

As a consequence, the search for elastomers that can be adapted for AM has attracted significant research attention in recent years, and among possible candidates polysiloxanes (often referred to as "silicones") play a major role because of their unique and exceptional combination of physical and chemical properties that make them some of the best rubbers known to polymer science.[5,6] Serious advances in this field have been reported by various research groups, including Plott and Shih,[7,8] *Sirrine, Williams, Long et al. (UV-activated thiol-ene addition cure),[9] Zheng and Brook,[10] a group from Lawrence Livermore National Laboratory (thermally induced hydrosilylation cure),[11] and researches from Wacker Chemie AG,[12-14] and Dow Corning.[15] (UV-activated cure).[5]

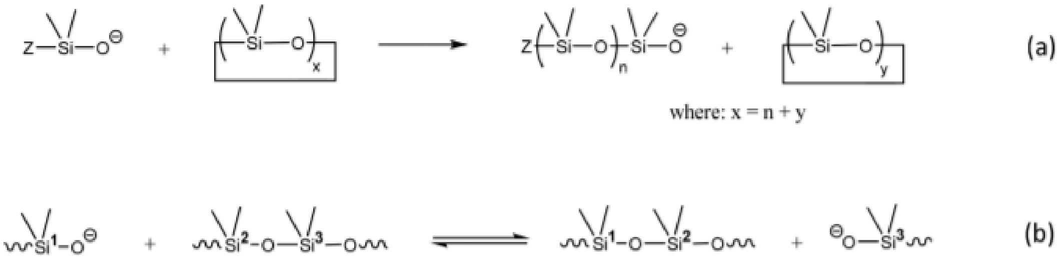
1.3 Polysiloxanes:

Polysiloxanes are very popular organic-inorganic polymers used currently in every day's life and industry for a wide range of applications. The primary reason for this is their outstanding combinations of high temperature stability, high flexibility at low temperatures, unique surface properties (non-stick and non-wetting properties, particularly in fluorinated derivatives), insulating ability, biocompatibility, and high resistance to weather and many chemicals.[16]

As a consequence, they are of high interest as elastomers to be used in AM. However, to satisfy the purpose, the polysiloxane "inks" (or pastes as referred to in this work) need to possess another combination of properties specifically designed for use in AM prior to permanent curing, including: adjustable thixotropy, easy handling, prolonged shelf-life stability, and fast and complete UV-activated crosslinking (curing), preferably at room temperature in air.[17] If the balancing of such a unique combination of properties can be achieved, the resulting polysiloxanes would provide for a wide range of adjustability to accommodate requirements of varies types of AM techniques for specific high quality rubber parts. Among polysiloxanes, fluorosiloxanes would become highly desirable members of the family, due to their ability to add to the above-mentioned well-known properties of non-fluorinated polysiloxanes, more fluoro-specific benefits such as a low surface energy (non-stick surfaces) and more pronounced hydrophobicity (non-wetting).[18]

1.4 Polysiloxane Synthesis

Polysiloxanes can be prepared in several different ways,[16] of which anionic ring-opening polymerization (A-ROP) of cyclic siloxanes using silanolate-initiators is a very convenient one.[16] It is a complex process that consists of two parallel, simultaneous reactions: (a) A-ROP of cyclic monomers and (b) the siloxane equilibration (redistribution) reaction, (SER), as shown in a generalized example in Reaction Scheme 1.1. In the process, nucleophilic silanolate anions (from either silanolate A-ROP initiator or silanolate growing polymer active centers) react with siloxane bonds present in either cyclic or linear components of the reaction system, so that both polymer growing reaction (A-ROP) and molecular size randomization reaction (SER) occur either simultaneously or successively depending on their specific kinetic parameters.[19]



Scheme 1.1: Generalized Scheme of A-ROP and SER Reactions Occurring in a Silanolate-Initited Syntheis of Polysiloxanes

1.5 Past work

In order to meet the strict requirements of AM for successful 3D printing with silicone pastes outlined above, we have developed a new approach toward polymer structure design, polymer synthesis and subsequent compounding into thixotropic *"all-in-one"* (A-1/P) silicone pastes that have long shelf lives, appropriate rheology for DIW printing and are capable of quick and permanent shape fixing of printed objects via fast and efficient crosslinking by UV-activated hydrosilylation in air at room temperature.[5]

The first established key findings were that suppression of crystallization in polydimethylsiloxanes (PDMS) and thus extension of high level of flexibility of their elastomers all the way to the polymer glass temperature of around -125 ^{o}C was possible with addition of small amounts (around 7 mol % or smaller) of crystallization disrupting repeat units, such as diphenylsiloxy (DiPhS), methylphenylsiloxy (MePhS) or diethylsiloxy (DiEtS) into the PDMS chains, and that chain branching in phenyl-containing polymers occurred under the synthetic conditions used unless special precautions were undertaken. To test this, four groups of polydimethylioxane terpolymers, containing 5 mol % of either DiPhS or DiEtS, with a DP range from 80 to 600 were synthesized. It was found that only 3.6 mol % DiPhS or 5 mol % DiEtS were sufficient to completely suppress crystallinity (as determined by differential scanning calorimetry, DSC).[20]

The next major contribution to this polymer synthesis was of ways to actively monitor the reaction progress. This is a complex reaction that takes careful timing and heat control to achieve sufficient opening of cyclic species to complete the polymerization. Monitoring was done by subjecting samples to thermogravimetric analysis (TGA), size-exclusion chromatography (SEC), and silicon nuclear magnetic resonance (^{29}Si NMR) in order to determine the rate of consumption of the reagents and their conversion into useful high molecular weight (MW) polysiloxanes. This experiment also showed that both the D_4 homopolymerization and the D_4 and D_3^{Et} copolymerization reactions behave and progress in a similar fashion. However, this was not the case for the reaction containing D_4 and D_4^{DiPh} due to the insolubility of the solid D_4^{DiPh} monomer in a D_4-dominated reaction mixture prior to the addition of the TMAS initiator.[19]

With this new understanding of the terpolymer’s synthesis and structure-property relationships, the next step was to develop the A-1/Ps. The three types of pastes produced in this study contained all necessary components to enable a fast and permanently cross-linked elastomer for AM under the conditions typically used in DIW. It was discovered that by adjusting the amount of silica filler and thixotropic agent, the thixotropic flow behavior could be fine-tuned to a desired yield stress appropriate for DIW. It was also discovered that if properly stored (refrigerated and kept away from excess ambient light) the pastes could last over six months.[21]

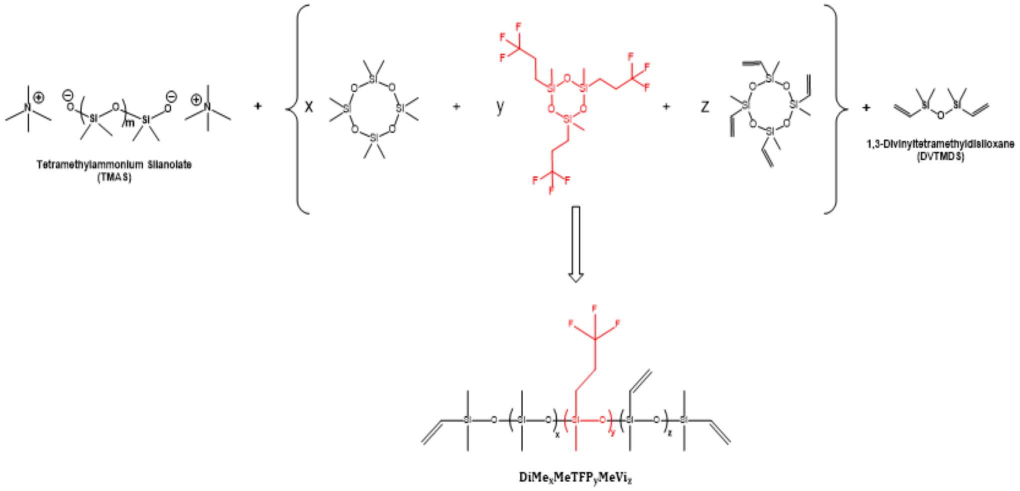
Lastly, the group monitored how much the molecular weight of methylphenylsiloxy (MePhS-) containing terpolymers affected the overall functionality and ability to crosslink A-1/Ps. It was found that the molecular weight of terpolymers had no significant effect on the rheological abilities of the pastes, but rather the relative amounts of silica filler and thixotropic additive were the sole influence. An inverse correlation between the MW of the bulk polymer used in a paste and the UV curing time was also discovered. Lastly, the (unexpected) appearance of strain induced crystallinity (SIC) was also noted via DMA in elastomers made from polysiloxanes with a DP of 240 or higher, indicating that there is a critical length of network chains between 160 and 240 DP where this phenomenon occurs. To the group's knowledge this was the first-time the network chain length dependent SIC has been reported occurring in polysiloxane elastomers.[17]

CHAPTER II

RESULTS AND DISCUSSION

2.1 Polymers

All terpolymers of this work were prepared (as described in the experimental section on page 47) by an anionic ring opening polymerization (A-ROP) with equilibration of mixtures of cyclic siloxanes including octamethylcyclotetrasiloxane ($[Si(CH_3)_2)O]_4$-, D_4), 1,3,5-Tris[(3,3,3-triffluoropropyl)methyl]cyclotrisiloxane ($[Si(CH_3)(CH_2CH_2CF_3)O]_3$-, D_3^{MeTfpS}) and 2,4,6-tetramethyltetravinylcyclotetrasiloxane ($[Si(CH_3)(CH=CH_2)O]_4$-, D_4^{MeVi}), as shown in Reaction Scheme 2.1. The A-ROPs were initiated by an oligomeric (m = 11) difunctional α,ω-telechelic tetramethylammonium, dimethylsilanolate (TMAS), in the presence of divinylteramethyldisiloxane, CH_2=CH-$Si(CH_3)_2$-O-$Si(CH_3)_2CH$-=CH_2 (DiViEB) molecular weight regulator and end-blocker. Two groups of terpolymers (labeled $DiMe_xMeTfp_yMeVi_z$ in Reaction Scheme 2.1 and referred to here as MeTfpS-containing terpolymers were prepared (see Tables 2.1 and 2.2). The first consisted of 6 terpolymers targeted to contain 5 mol % of MeTfpS repeat units with varying degrees of polymerization (DP) from 80 to 600; these terpolymers have the same overall composition (x = 0.947; y =0.05; and z = 0.003) and are coded herein as A through F (Table 2.1). The second group of terpolymers contained 3 terpolymers with varying amounts of MeTfpS repeat units (5%, 10%, and 15% mol %, respectively) but the same targeted DP of 600, and are coded here as A, G, and H, respectively (Table 2.2).



Where y = 5, 10 or 15 mol%

Scheme 2.1: Synthesis of MeTfpS-Containing Terpolysiloxanes of this work via A-ROP with equilibration

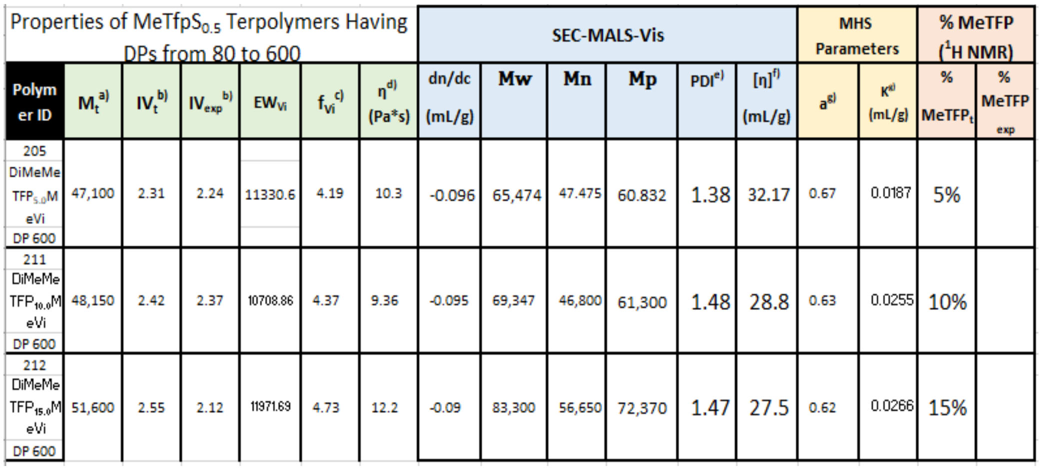
Selected properties of the prepared polymers are summarized in Tables 2.1 and 2.2. For all samples. SEC-MALS-VIS showed very close to expected values for targeted molecular weights (M_n), with chromatograms having clean monomodal distributions with polydispersity indexes (PDI = M_w/M_n) being in the range of 1.38-1.48 (typical for A-ROP with equilibration) (see Figure 2.1), and Mark-Houwink-Sakurada (MHS) exponents (a) all around 0.65-0.70, typical for liner polymers in thermodynamically good solvents (see Figure 2.2).

Table 2.1: Selected Properties of 5.0 mol % MeTfpS-Containing Terpolysiloxanes with Varying Degrees of Polymerization (DP)

Properties of MeTfpS$_{0.5}$ Terpolymers Having DPs from 80 to 600							SEC-MALS-Vis						MHS Parameters		% MeTFP (^{1}H NMR)	
Polymer ID	M$_t$ a)	IV$_t$ b)	IV$_{exp}$ b)	EW$_{Vi}$	f$_{Vi}$ c)	η d) (Pa*S)	dn/dc (mL/g)	Mw	Mn	Mp	PDI e)	[η] f) (mL/g)	a g)	K g) (mL/g)	% MeTFP$_t$	% MeTFP$_{exp}$
205 DiMeMeTFP$_{5.0}$MeVi DP 600	47,100	2.31	2.24	11330.6	4.19	10.3	-0.096	65,474	47.475	60.832	1.38	32.17	0.67	0.0187	5%	
206 DiMeMeTFP$_{5.0}$MeVi DP 480	37,800	2.6	2.19	11589	3.11	4.73	-0.099	49.308	35.985	47.897	1.37	27.06	0.69	0.0198	5%	
207 DiMeMeTFP$_{5.0}$MeVi DP 360	28,400	3.09	2.79	9096.77	2.07	0.738	-0.094	26.027	18.855	24.365	1.38	15.19	0.66	0.0185	5%	
208 DiMeMeTFP$_{5.0}$MeVi DP 240	19,000	4.06	4.35	5834.48	3.39	0.98	-0.093	28.249	19.76	26.952	1.43	17.04	0.068	0.0193	5%	
209 DiMeMeTFP$_{5.0}$MeVi DP 160	12,700	5.52	4.55	5578.02	2.52	0.56	-0.095	20,129	14,079	18.893	1.43	13.77	0.67	0.0141	5%	
210 DiMeMeTFP$_{5.0}$MeVi DP 80	6,450	9.9	7.04	3605.11	1.93	0.15	-0.091	9,706	6,958	9.545	1.4	7.79	0.69	0.0188	5%	

a)M$_t$: targeted molecular weight; b)IV$_t$ and IV$_{exp}$: iodine values theoretical and experimental, respectively, c)$f_{vi} = M_n/EW_{vi}$. The eight of Vi equivalent; EW_{Vi} = MW (I$_2$) x 100/IV = 25360/IV; d)η: dynamic viscosity of isolated polymers as determined by cone and plate viscometry; e) PDI: polydispersity index; PDI = M$_w$/M$_n$; f) [η]: intrinsic viscosity as determined by Visco Star II online detector; g) a and K: parameters of Mark-Houwink-Sakurada equation: [η] = K M^a. For linear, flexible polymers in thermodynamically good solvents a is usually 0.7.

Table 2.2: Selected Properties of DP = 600 MeTfpS-Containing Terpolysiloxanes with 5, 10 and 15 mol% of MeTfpS Repeat Units



Properties of MeTfpS$_{0.5}$ Terpolymers Having DPs from 80 to 600							SEC-MALS-Vis						MHS Parameters		% MeTFP (^{1}H NMR)	
Polymer ID	M$_t$$^{a)}$	IV$_t$$^{b)}$	IV$_{exp}$$^{b)}$	EW$_{Vi}$	f$_{Vi}$$^{c)}$	η$^{d)}$ (Pa*s)	dn/dc (mL/g)	Mw	Mn	Mp	PDI$^{e)}$	[η]$^{f)}$ (mL/g)	a$^{g)}$	K$^{g)}$ (mL/g)	% MeTFP$_t$	% MeTFP$_{exp}$
205 DiMeMeTFP$_{5.0}$MeVi DP 600	47,100	2.31	2.24	11330.6	4.19	10.3	-0.096	65,474	47.475	60.832	1.38	32.17	0.67	0.0187	5%	
211 DiMeMeTFP$_{10.0}$MeVi DP 600	48,150	2.42	2.37	10708.86	4.37	9.36	-0.095	69,347	46,800	61,300	1.48	28.8	0.63	0.0255	10%	
212 DiMeMeTFP$_{15.0}$MeVi DP 600	51,600	2.55	2.12	11971.69	4.73	12.2	-0.09	83,300	56,650	72,370	1.47	27.5	0.62	0.0266	15%	

a) M$_t$: targeted molecular weight; b) IV$_t$ and IV$_{exp}$: iodine values theoretical and experimental, respectively, c) $f_{vi} = M_n/EW_{vi}$. The eight of Vi equivalent; EW_{Vi} = MW (I_2) x 100/IV = 25360/IV; d) η: dynamic viscosity of isolated polymers as determined by cone and plate viscometry; e) PDI: polydispersity index; PDI = M$_w$/M$_n$; f) [η]: intrinsic viscosity as determined by Visco Star II online detector; g) a and K: parameters of Mark-Houwink-Sakurada equation: [η] = K M^a. For linear, flexible polymers in thermodynamically good solvents a is usually 0.7.

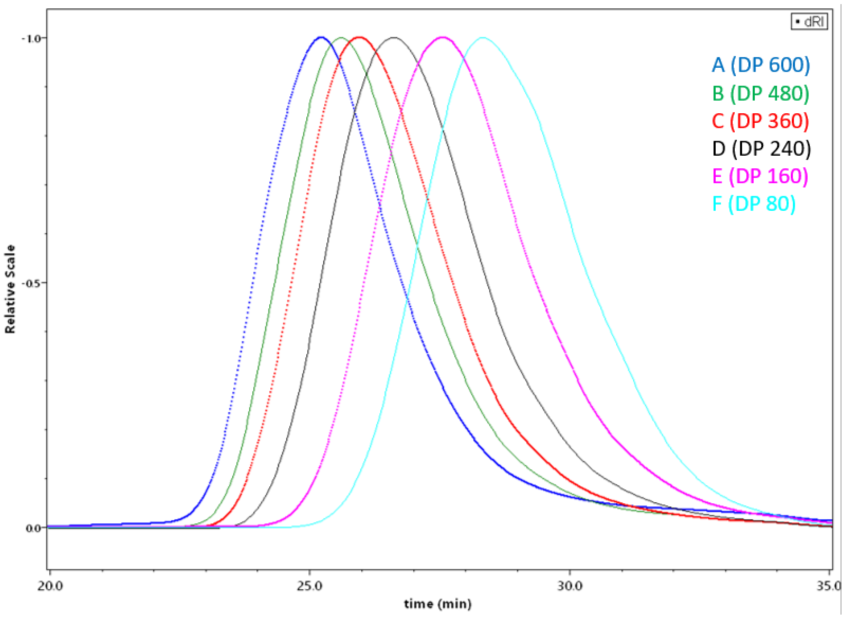


Figure 2.1 SEC traces of 5 mol % MeTfpS-Containing Terpolysiloxanes with Varied DPs from 80 to 600.

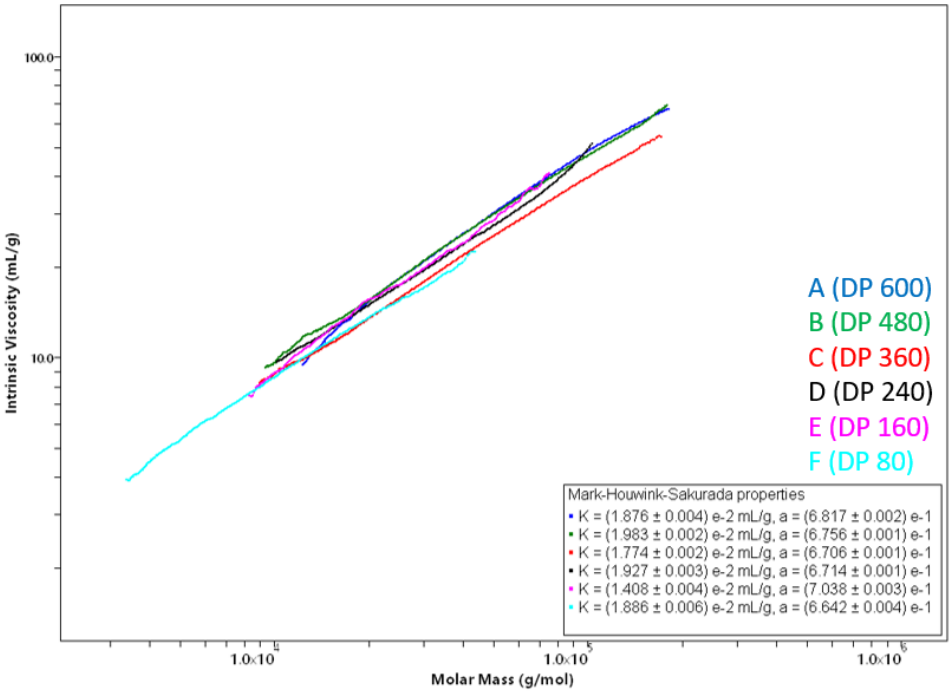


Figure 2.2 Mark-Houwink-Sakurada Plots for 5 mol % MeTfpS-Containing Terpolysiloxanes with Varying DP from 80 to 600.

DSC data showed that, as expected, all terpolymers were completely amorphous in character (as indicated by the absence of crystallization/melting transitions typically observed for polydimethylsiloxanes (PDMS) between -50 and -40 ^{o}C); (see Figure 2.3 and 2.4) and TGA thermograms (see Figures 2.5 and 2.6) exhibited well-known high thermal stability characteristic for PDMS and PDMS-like polymers.[22,23]

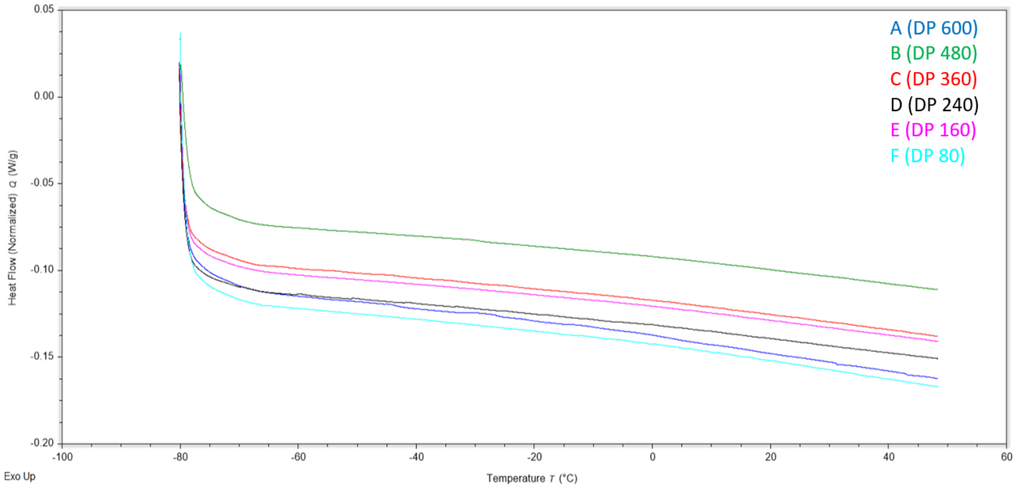


Figure 2.3: DSC Traces of 5 mol % MeTfpS-Containing Terpolysiloxanes with Varied DPs from 80 to 600.

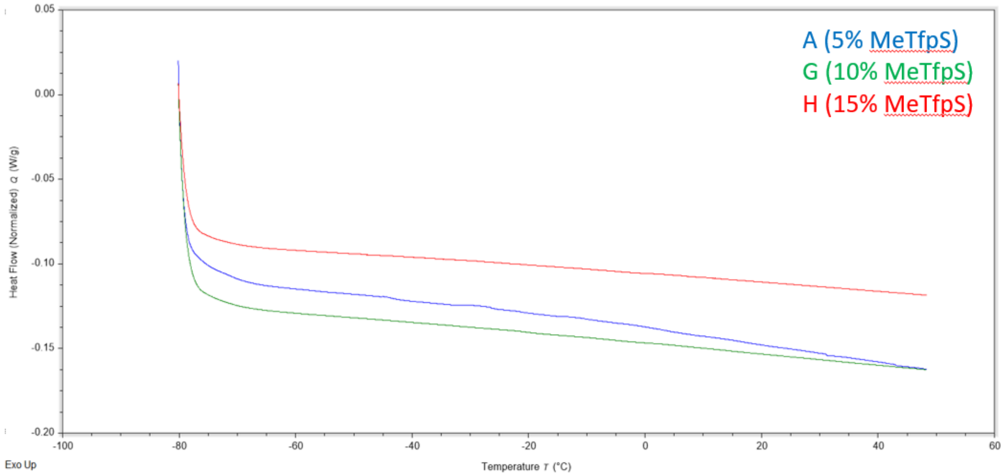


Figure 2.4: DSC traces of DP = 600 MeTfpS-Containing Terpolysiloxanes with 5, 10 and 15 mol% of MeTfpS Repeat Units.

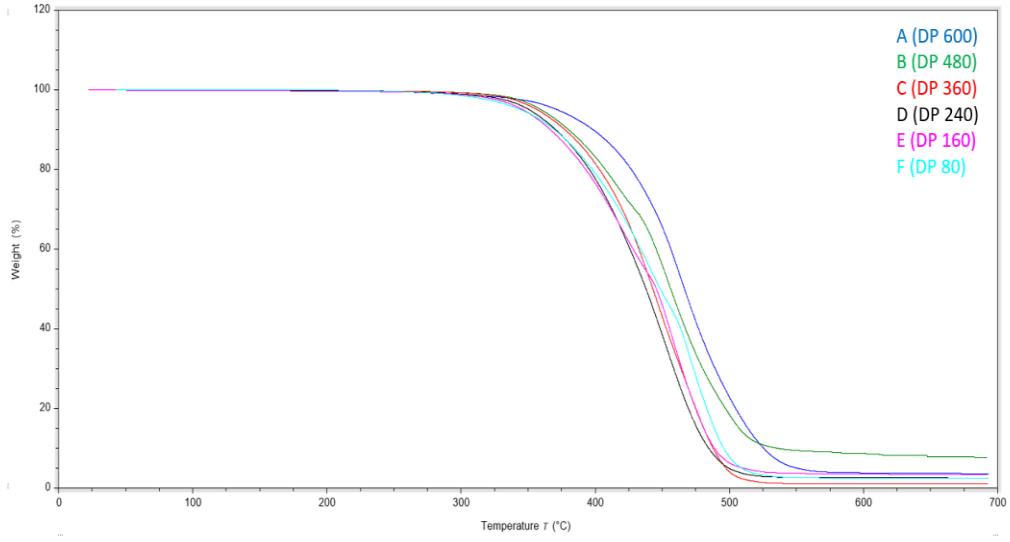


Figure 2.5: TGA traces of 5% MeTfpS-Containing Terpolysiloxanes with Varying DPs from 80 to 600.

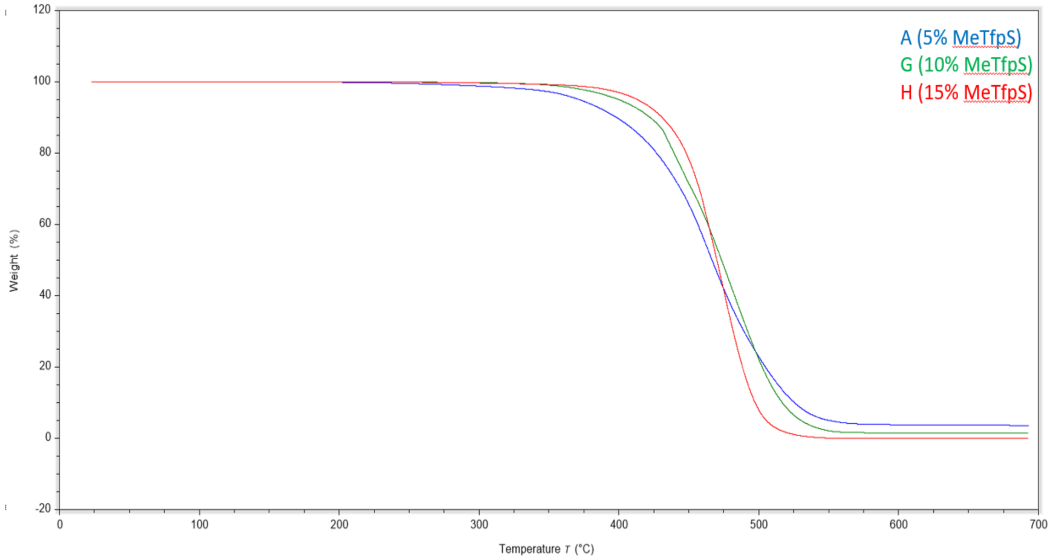


Figure 2.6: TGA traces of 5, 10, and 15% MeTfpS-Containing Terpolysiloxanes with DP of 600.

2.2 Monitoring of the Polymerization Reactions of MeTfpS-Containing Terpolymers

All terpolymer syntheses performed in this work were monitored by both SEC and TGA to follow in real time the increase in polymer molecular weights and monomer conversions, respectively.[19] Also, the removal of cyclic material could be observed in respective TGA traces (by disappearance of the weight-loss in the temperature ranges from room temperature to about 175 ^{o}C caused by evaporation of the lower molecular weight cyclics during the distillation procedures and subsequent polymer precipitation), as illustrated in Figure 2.7.

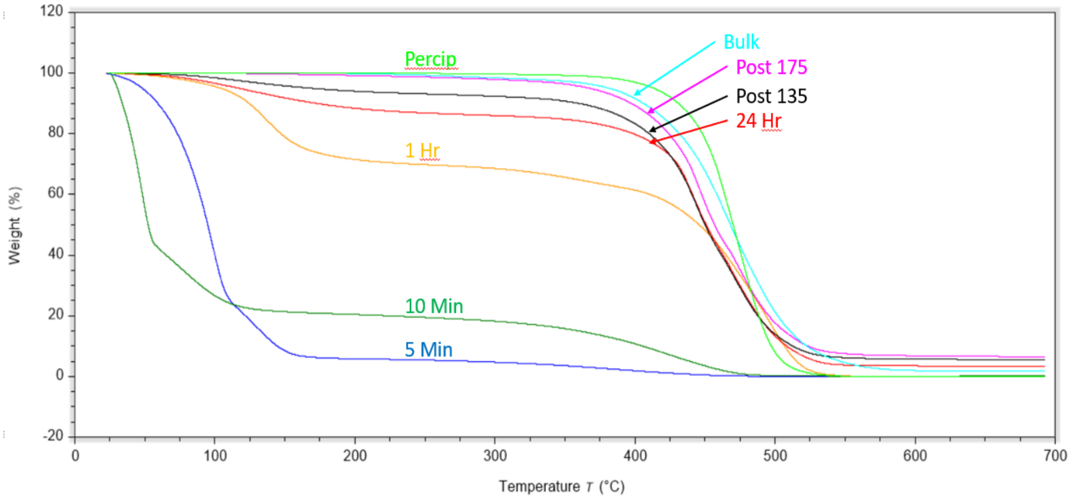


Figure 2.7: TGA Monitoring of the Synthesis of 15 mol % MeTfpS-Containing Terpolysiloxanes with a DP of 600

2.2.1 Monitoring of the Polymerization Reactions by SEC with Toluene as Eluent

Syntheses of all eight terpolymers prepared in this work were monitored by SEC, using toluene as the eluent. Figure 2.8 illustrates this procedure for the synthesis of Polymer A throughout the entire A-ROP reaction. All eight-syntheses showed similar features: intense sharp signals at 37-40 min retention times which depleted over time as cyclic monomers were being consumed in the A-ROP; broad and intense signals from the growing polymers at 23-31 min retention times; and small, multiplet side signals to the former at 37-39 min retention times from oligomeric cyclics being formed during the A-ROP reactions as by-products. Both polymer signals and reaction-formed oligomeric cyclic signals can be seen appearing after about 15 minutes of reaction time, while the targeted MW of the 5 mol % MeTfpS-containing polymer was obtained after only 30 mins. Appendix (Chapter VI starting on page 61) contains corresponding SEC monitoring figures for all other polymers prepared. It can be seen from these figures that as the targeted DP values of other 5 mol % MeTfpS-containing terpolymers were decreased, the targeted MWs were reached faster, taking only 10 mins of reaction time for polymers with DPs of 240 or lower. A similar feature was also observed for the 10% and 15% MeTfpS-containing terpolymers, where the higher the percentage of D_3^{MeTfpS} was in the terpolymer the faster the targeted MW was reached.

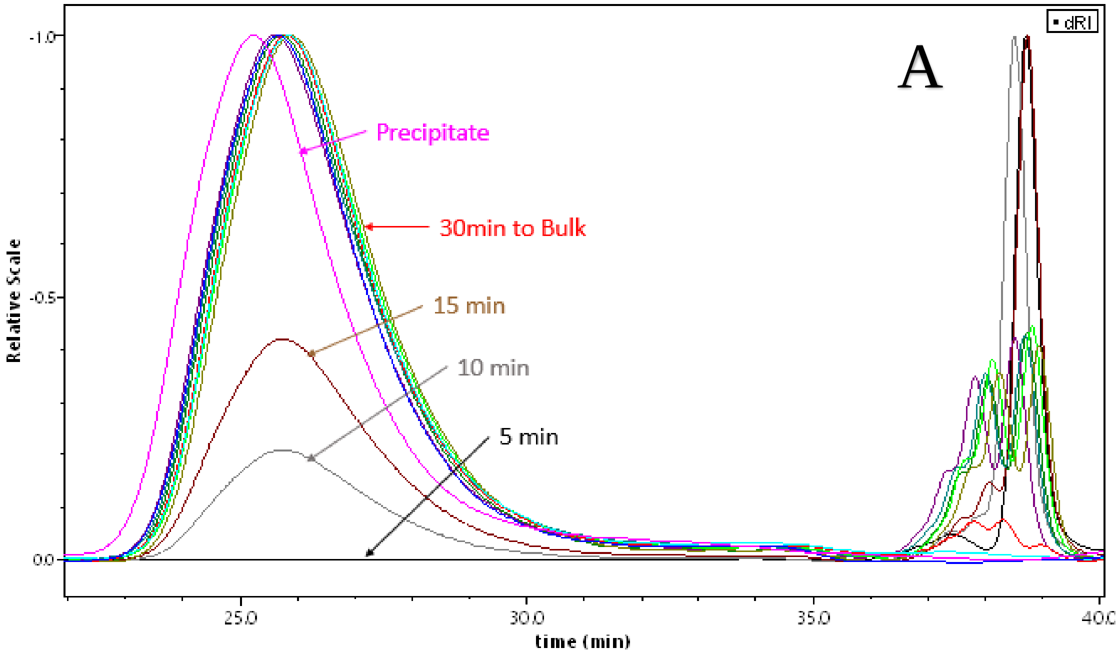


Figure 2.8: SEC Monitoring of the Synthesis of 5% MeTfpS-Containing Terpolysiloxane A Having Targeted DP of 600.

Utilizing all monitoring data obtained in this work, the increase in polymer molecular weights with the reaction times for all eight terpolymer syntheses performed are shown in Figures 2.9 and 2.10. It can be seen from these figures that all terpolymers reached their targeted molecular weights in less than 10 min of reaction times (consistent with fast A-ROP) and that no further increase in the polymer molecular weight occurred if more reaction time was allowed. Additionally, neither the degree of polymerization nor the targeted mol % of D_3^{MeTfpS} used seemed to significantly affect this behavior.

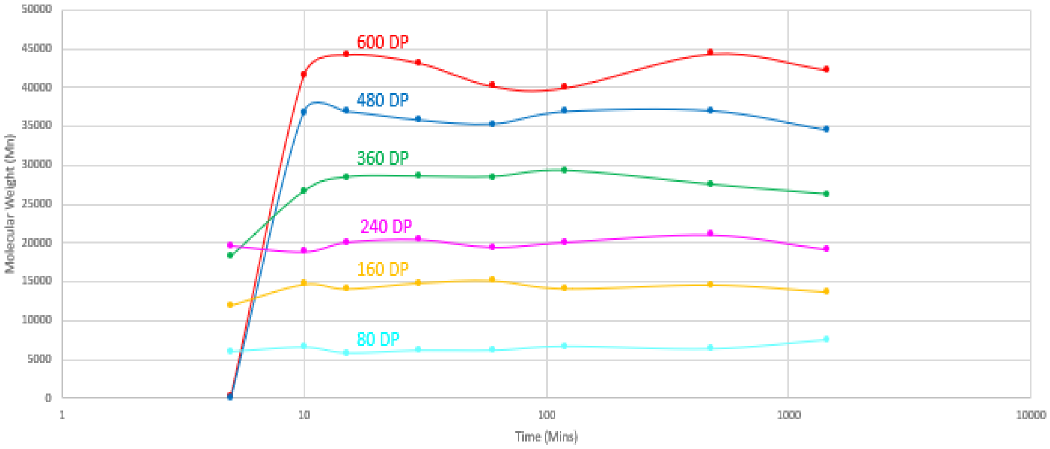


Figure 2.9: Molecular Weight vs Polymerization Reaction Time for the Syntheses of MeTfpS-Containing Terpolysiloxanes with Varying DPs from 80 to 600.

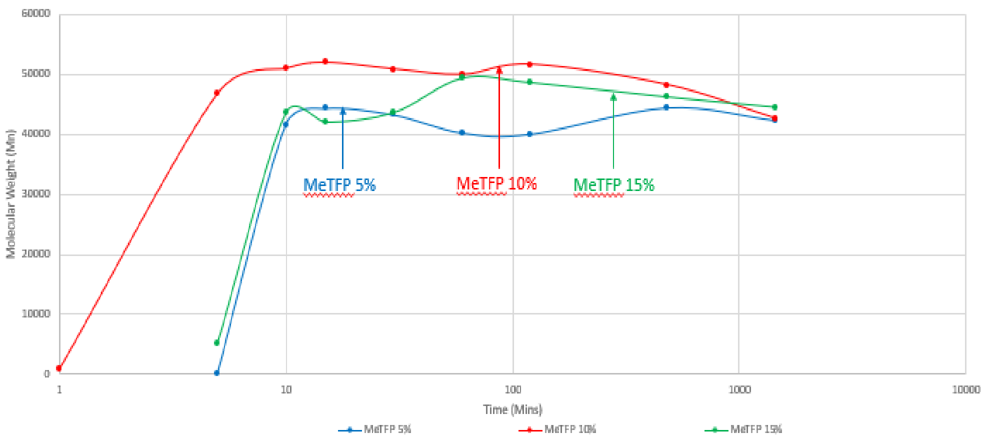


Figure 2.10: Molecular Weight vs Polymerization Reaction Time for the Syntheses of MeTfpS-Containing Terpolysiloxanes of DP = 600 and Varying Content of MeTfpS Repeat Units

Furthermore, in order to gain better understanding of the syntheses of these MeTfpS-containing terpolysiloxanes, the obtained monitoring data for Polymer A (DP=600 and 5 mol % MeTfpS) were compared with the data previously published by the Dvornic group for the corresponding all-DiMeS-containing polymer, and DiPhS-, MePhS-, and DiEts-containing terpolymers with minimal amounts of the crystallization-preventing repeat units,[17] and the obtained results are shown in Figure 2.11.

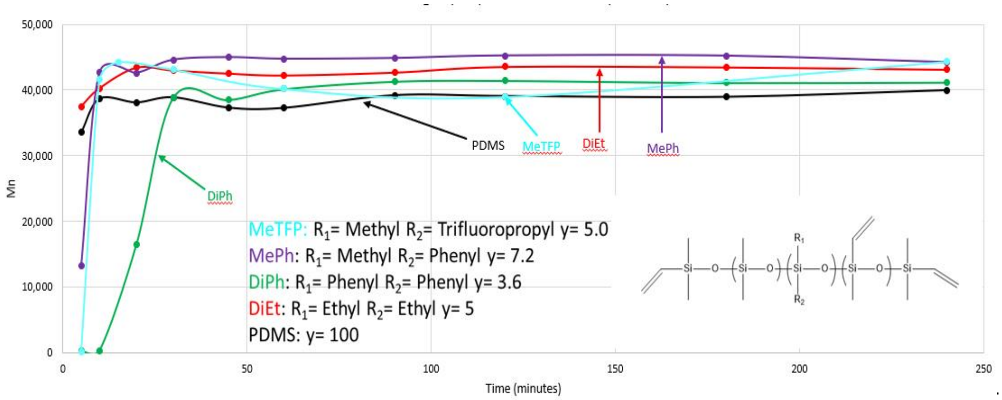


Figure 2.11: Molecular Weight vs Polymerization Reaction Time for the Syntheses of Terpolysiloxanes of Varying Type of Crystallization Preventing Repeat Units with Comparable DPs and Relative Content of the Crystallization Preventing Repeat Units

As expected, the MeTfpS-containing terpolymers behaved very similarly to the corresponding DiMeS-, MePhS-, and DiEtS-containing terpolymers variants, with only the DiPhS-containg terpolymer showing the characteristic inhibition period due to the low solubility of its cyclic monomer in D_4 [17].

2.2.2 Monitoring of the Polymerization Reactions by TGA

The TGA, while usually used to observe thermal and thermo-oxidative stability behaviors of investigated samples, was used in this work to follow the increasing yield of the polymer products during the respective courses of their polymerization reactions, and to distinguish between smaller, volatile cyclics and oligomers, larger, and non-volatile, high molecular weight polymers that were both being formed during the process. Figure 2.12 illustrates one such monitoring procedure, using Polymer A as an example. The distinct behaviors of two reaction products can be easily seen in two different temperature ranges. At temperatures below 160-175 ˚C, a sharp weight drop can be observed in the 5- and 10-min samples, corresponding to the evaporation of low boiling point components (starting material and reaction-formed cyclics) during the TGA experiment, while at temperatures above 180-200 ^{o}C, there was only a plateau in sample weight, consistent with TGA patterns typical for PDMS with no leftover initiator from the polymerization reaction corresponding to the relative amount of open-chain polymer formed.

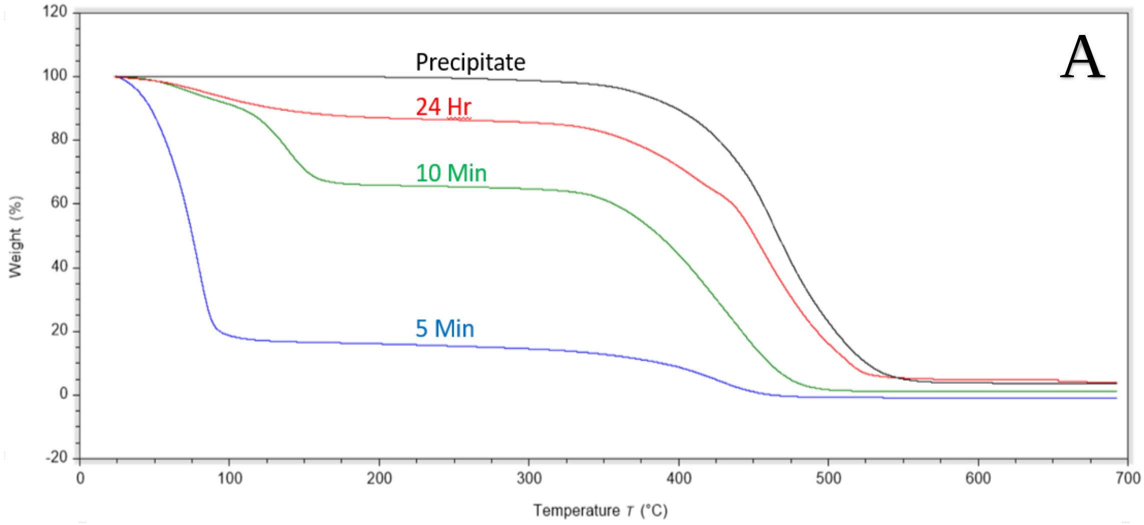


Figure 2.12: TGA Monitoring of the Synthesis of 5% MeTfpS-Containing Terpolysiloxane A Having Targeted DP of 600.

Utilizing all TGA monitoring data (see Appendix pages 64-67) the increase of polymer yields with reaction times for all 8 terpolymers synthesized in this work are summarized in Figures 2.13 and 2.14. It can be seen from these figures that all reactions were nearing completion after about 60-100 min, with only a slight increase in the amount of polymer formed if further reaction time was permitted. Additionally (with a possible outlier being the 5 mol % MeTfpS-containing polymer with DP = 240), neither the degree of polymerization nor the targeted mol % of D_3^{MeTfpS} used seemed to significantly affect the overall polymer yields obtained.

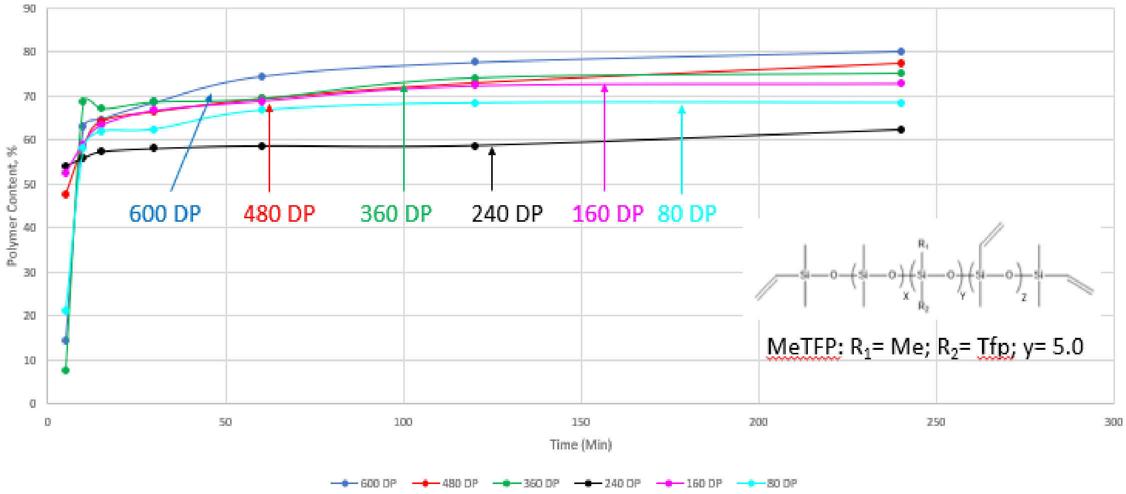


Figure 2.13: Terpolysiloxane Yield vs Polymerization Reaction Time for the Syntheses of MeTfpS-Containing Terpolysiloxanes with Varying DPs from 80 to 600.

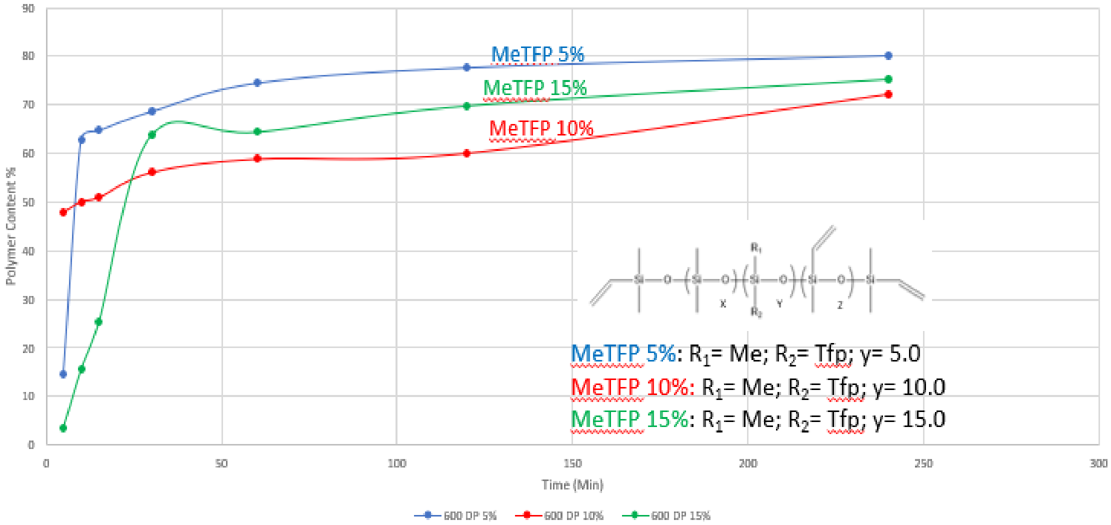


Figure 2.14: Terpolysiloxane Yield vs Polymerization Reaction Time for the Syntheses of MeTfpS-Containing Terpolysiloxanes of DP = 600 and Varying Content of MeTfpS Repeat Units

Utilizing the information gathered from the past work [19,20], we have compared the above-described data with the TGA monitoring results from the syntheses of the corresponding DiPhS-, MePhS- and DiEtS-containing terpolysiloxane counterparts (see Figure 2.15). This comparison shows that in all cases, the reactions were practically complete after 175-200 minutes, consistent with relatively small contents of crystallization disrupting units in a predominantly PDMS-like compositions. A notable induction period characteristic for the synthesis of DiPhS-Containing Terpolysiloxane can also be seen.

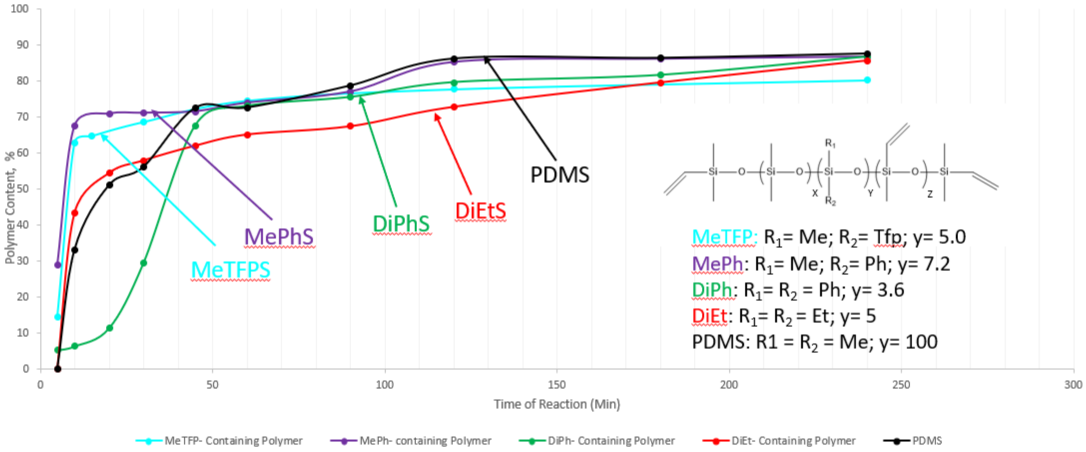


Figure 2.15: Terpolysiolxane Yield vs Polymerization Reaction Time for the Syntheses of Terpolysiloxanes with Varying Types of Crystallization Preventing Repeat Units with Comparable DPs and Relative Content of the Crystallization Preventing Repeat Units

2.3 *"All-in-One"* Polymer Pastes

All terpolymers described above were used for preparation of *"all-in-one"* (A-1/P) silicone pastes for application in AM by DIW technology.[5] The name given above to these pastes is meant to reflect that they contain all necessary components for simple, practical and efficient printing followed by quick and simple permanent shape fixing after the printed object formation. Their components include: base terpolysiloxanes (i.e., the above described vinyl-functionalized terpolysiloxanes); crosslinking agent (i.e., hydride-functionalized silicone oligomer); UV-activated hydrosilylation catalyst trimethyl(methylcyclopentadienyl)platinum(IV) (TMMCpPt); thixotropic agent (i.e., Thixo Add 22646 thixotropic additive); fumed (trimethylsilylated silica filler) and possibly (if desirable) other additives. They all have unique combination of properties, including: (*i*) long term shelf-life stability (over a year in some cases) enabling: (a) complete preparation/formulation at the paste producer's location, (b) convenient shipping to the printer and (c) ability to be stored at the printers site (even for extended periods of time) until final use; (*ii*) no need to be manipulated in any way by the printer (e.g., adding or combining more components than what was provided in the original all-in-one composition) in any way prior to use; (*iii*) excellent printability under selected printing conditions and ability to be specifically designed for those required; (*iv*) ability to transiently retain printed shape until permanent fixing; and (*v*) ability to rapidly covalently crosslink under UV irradiation in air and at room temperature to permanently fix the shape of the printed objects.

The pastes are prepared by "speed mixing" utilizing a duel asymmetric centrifuge mixer, as described in experimental section (Chapter 4, section 4.2.3). Image 2.1 shows one such example of an A-1/P after speed mixing in a plastic cup, and in the form of a hand-made shape to illustrate the ability of formed objects to transiently retain their shapes (thixotropy), as long as they are not exposed to any external stress (Image 2.2).

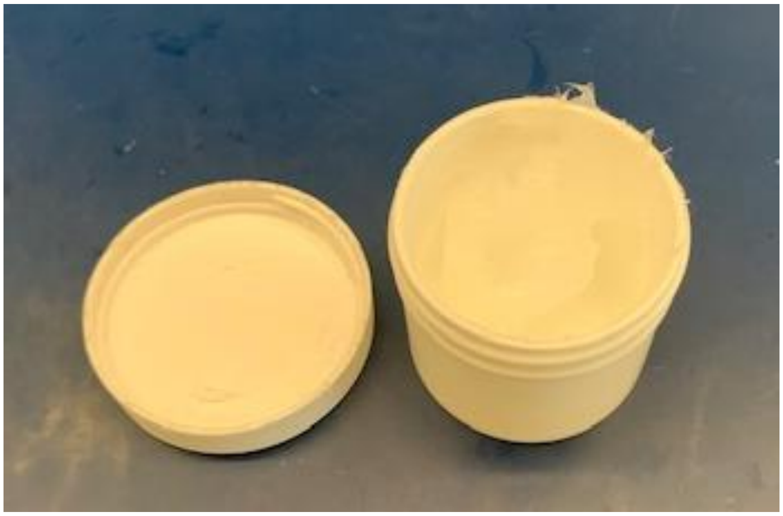


Image 2.1: A-1/P as obtained from speed mixing in a speed mixer cup

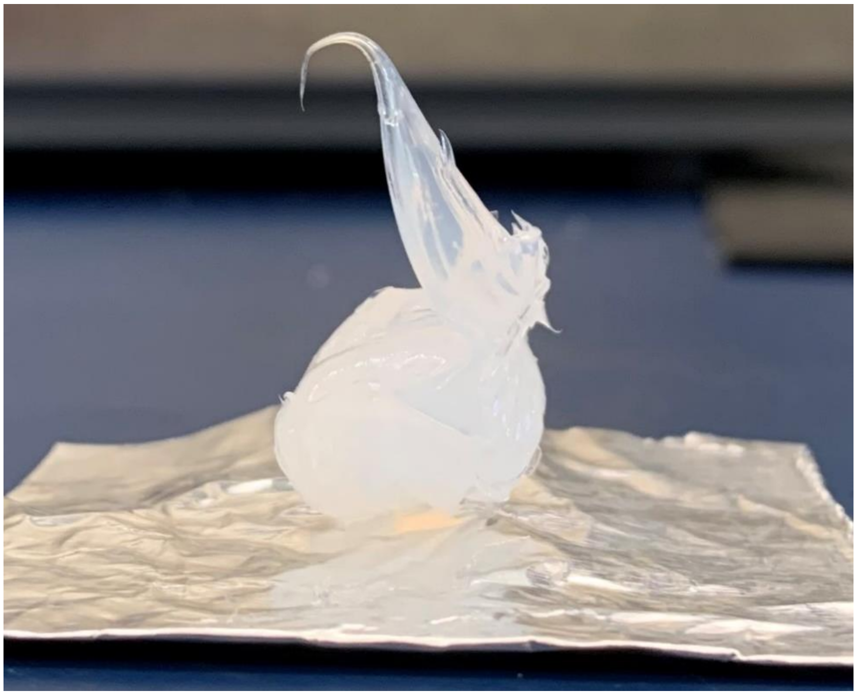


Image 2.2: A-1/P small hand formed object of the silicone paste retains its shape, as long as it is not exposed to external stress

2.4 A Year-Long Rheology Stability Study of A-1/Ps

Rheological properties of all eight non-crosslinking pastes were examined under steady and oscillatory shear weakly for one month, followed by monthly testing for an entire year (or until the pastes pre-maturely crosslinked or expired). Yield stresses (see Table 2.3 and Figure 2.18), thixotropic loops (see Figure 2.19**)** and storage moduli as a function of oscillatory stress (see Figure 2.20) for the series of pastes from 5 mol % MeTfpS-containing terpolymers A-F are shown below. Data for all individual samples are shown in Appendix starting on page 67. It can be seen from the data that all pastes demonstrated similar rheological properties and that varying DPs or amounts of MeTfpS repeat units did not affect these properties in any significant manner. This is consistent with the previous observation [21] that these rheological properties are determined by the filler component of the pastes rather than the terpolymers themselves. Data for Dow Corning Toray SE 1700 (a widely use silicon adhesive used as a standard for thixotropy comparisons) is also shown in Figure 2.19.

Table 2.3: Yield Stresses of 5% MeTfpS-Containing Terpolysiloxane Pastes from Polymers with Varying Degrees of Polymerization (DP) from 80 to 600.

	205 DP 600 (Pa)	206 DP 480 (Pa)	207 DP 360 (Pa)	208 DP 240 (Pa)	209 DP 180 (Pa)	210 DP 80 (Pa)
Day 0	2800	2700	2690	2560	1790	1630
Week 1	2830	1750	1500	1880	2020	1700
Week 2	2030	2615	1300	1690	1830	2100
Week 3	1520	1740	1330	2240	1790	2240
Week 4	2600	2700	2020	1230	1330	1670
Month 2	2500	2420	2030	1320	1690	1200
Month 3	2600	2400	1940	1080	1030	1320
Month 4	2600	2200	1910	870	1000	1190
Month 5	2450	2250	1900	1180	1350	1190
Month 6	2340	2200	1200	910	880	1150
Month 7	2300	2030	1090	850	1040	940
Month 8	2300	2100	750	920	1160	1170
Month 9	2270	2040	800	800	940	780
Month 10	2190	2050	940	910	1070	930
Month 11	2240	1916	1126	1130	1080	870
Month 12	2217	1985	730	1000	1020	1080

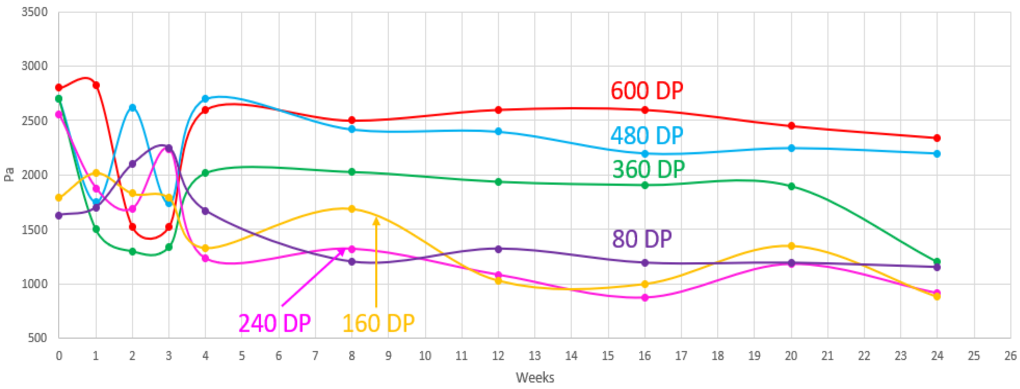


Figure 2.18: Long Term Oscillatory Shear Rheology Study of 5 mol % MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600. Storage Modulus (G’) as a Function of Paste Age.

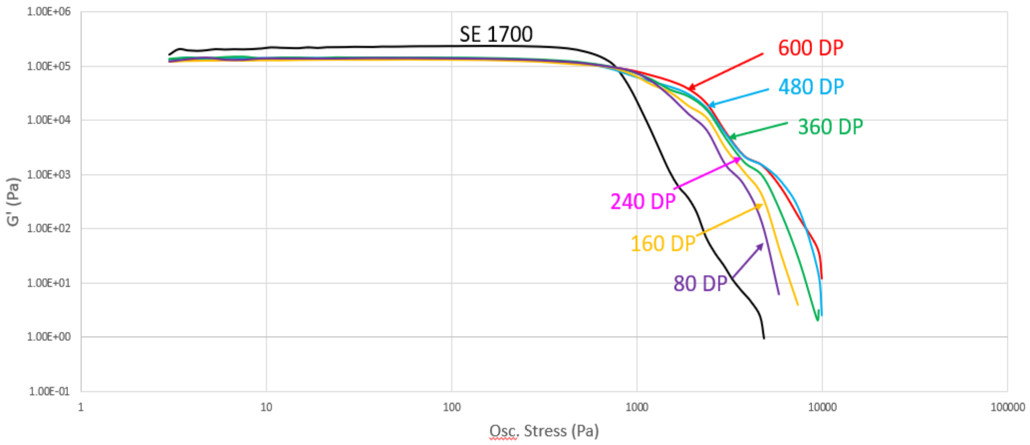


Figure 2.19: Oscillatory Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600 on the Day of Paste Preparation

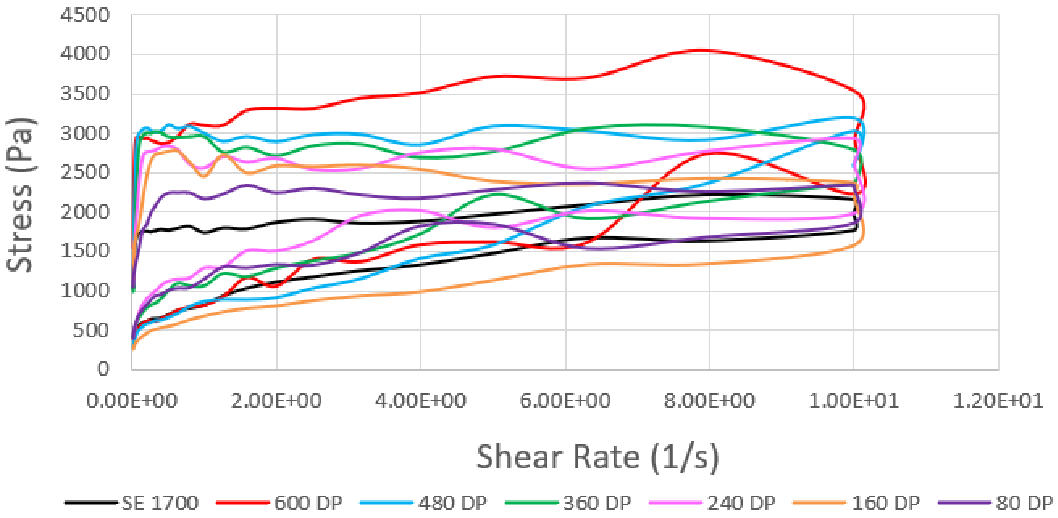
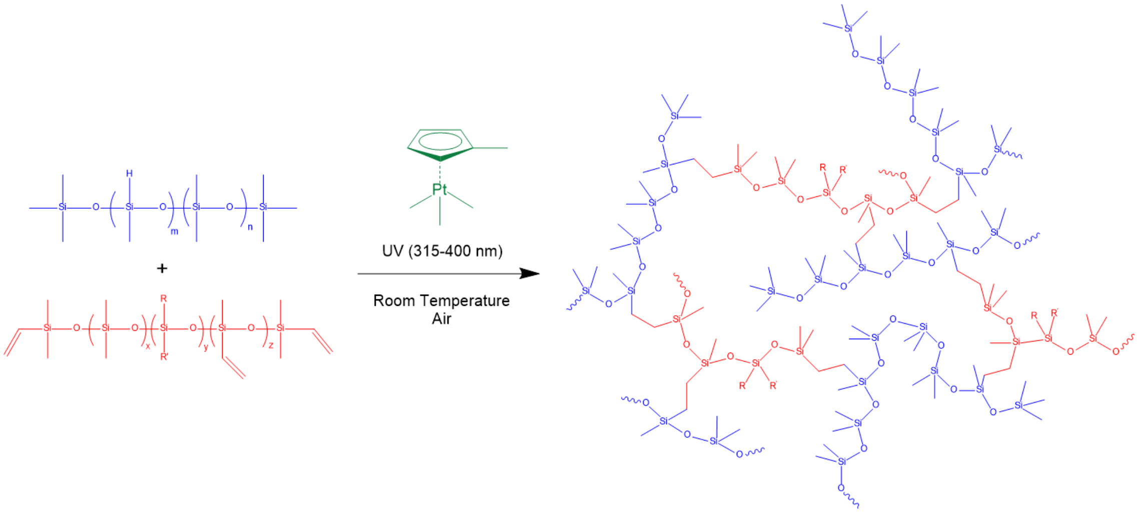


Figure 2.20: Steady Shear Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600 on the Day of Paste Preparation

Both the weekly and monthly tests showed that both oscillatory and steady shear responses of all examined pastes remained practically unchanged during the one year testing period (see Table 2.3).

2.5 Crosslinking of A-1/Ps

All "*all-in-one*" pastes described above (this time containing crosslinking agent and catalyst system in addition to the filler and thixotropic agent used above), were evaluated for crosslinking via UV-activated, TMMCP-catalysed hydrosilylation reaction at room temperature in air (see Reaction Scheme 2.2), and for a year long shelf-life stability study.



Scheme 2.2: UV-Activated Hydrosilylation Crosslinking of A-1/Ps Based on Vinyl-Functional MeTfpS-Containing Terpolysiloxanes.

The crosslinking (curing) was performed by casting the pastes in a rectangular (100 mm x 100 mm x 0.5 mm) and exposing them to UV-irradiation via a 400 W UV flood lamp (irradiance at 3" = 115 mW cm^{-2}). Samples were removed from the chamber containing the lamp every 5-10 seconds and prodded with a wooden stick to determine crosslinking progression, namely for the appearance of any tackiness that indicated partial or incomplete crosslinking. Once samples no longer exhibited any dimpling or tackiness, they were considered fully crosslinked. All samples were stored in an opaque plastic jar and kept in a fridge stored at 3-4 °C when not in use.

To further determine the extent (efficiency) of this crosslinking reaction, Soxhlet extraction (in tetrahydrofuran) were performed on all eight terpolymer elastomer samples using the procedure described in Chapter IV. The gel content for each terpolymer was recorded and shown in Table 2.4 below. It can be seen from this data that the crosslinking reactions were almost quantitative (i.e., 95-97 % complete) with only a 3-5% soluble sol fraction detected in the obtained polymer films.

Table 2.4: Gel Content (by Soxhlet Extraction) of Non-Filler, Non-Thixotropic Addatiative Containing Crosslinked Ealastomers from MeTfpS-Containing Terpolysiloxanes with Varying Degrees of Polymerization and MeTfpS Contents

Polymer	Weight Before (g)	Weight After (g)	Gel Content (%)
205 600 DP	1.158	1.124	97.0
206 480 DP	1.050	0.995	94.7
207 360 DP	1.646	1.600	97.2
208 240 DP	1.080	1.043	96.5
209 160 DP	0.956	0.923	96.5
210 80 DP	1.913	1.856	97.0
211 600 DP (10%)	1.145	1.102	96.2
212 600 DP (15%)	1.705	1.654	97.0

Figures 2.21 and 2.22 show cure times as a function of polymer molecular weight for the two series of MeTfpS-containing terpolymer pastes evaluated in this work, and a

comparison of the behavior of the 5 mol % MeTfpS-containing terpolymer based pastes with the corresponding MePhS-containing terpolymer pastes reported previously (see Figure 2.23).[17] It can be seen from Figure 2.21 in the 5 mol % MeTfpS-containing terpolymer series that the higher the terpolymer DP was, the faster the pastes crosslinked. This was due to higher concentration of the reacting Si-Vi groups present in the lower DP polymers and is consistent with the previously reported data for the corresponding MePhS-containing terpolymer based pastes.[17] It can also be seen from Figure 2.22 that in the DP = 600 series, it appears that, at constant degree of polymerization, the content of the MeTfpS repeat units did not significantly affect the rate of hydrosilylation crosslinking.

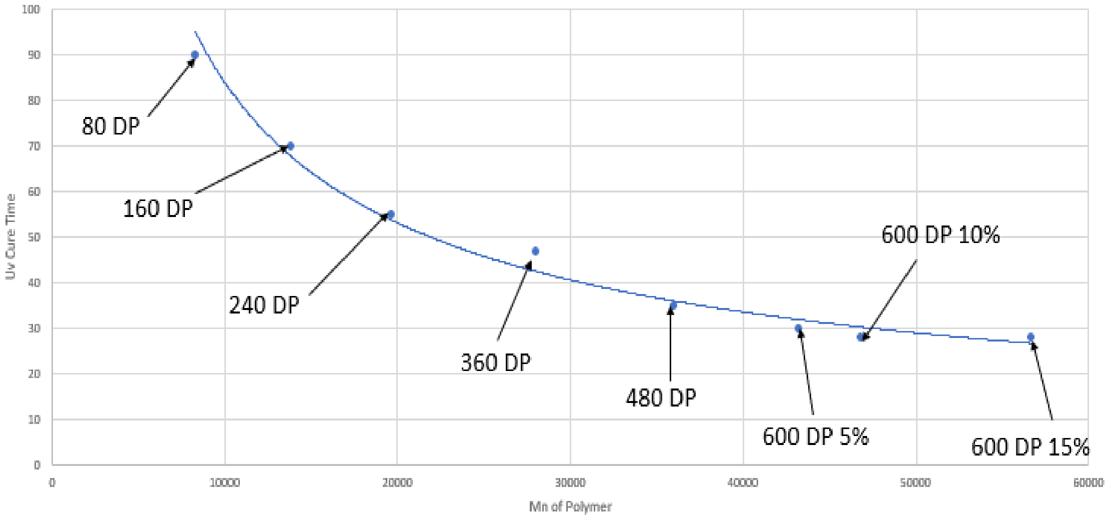


Figure 2.21: Dependence of the UV-Activated Cure Times of pastes from 5 mol % MeTfpS-Containing Terpolysiloxanes on the Polymer Molecular Weight for Varying Degree of Polymerization (DP) and MeTfpS Content.

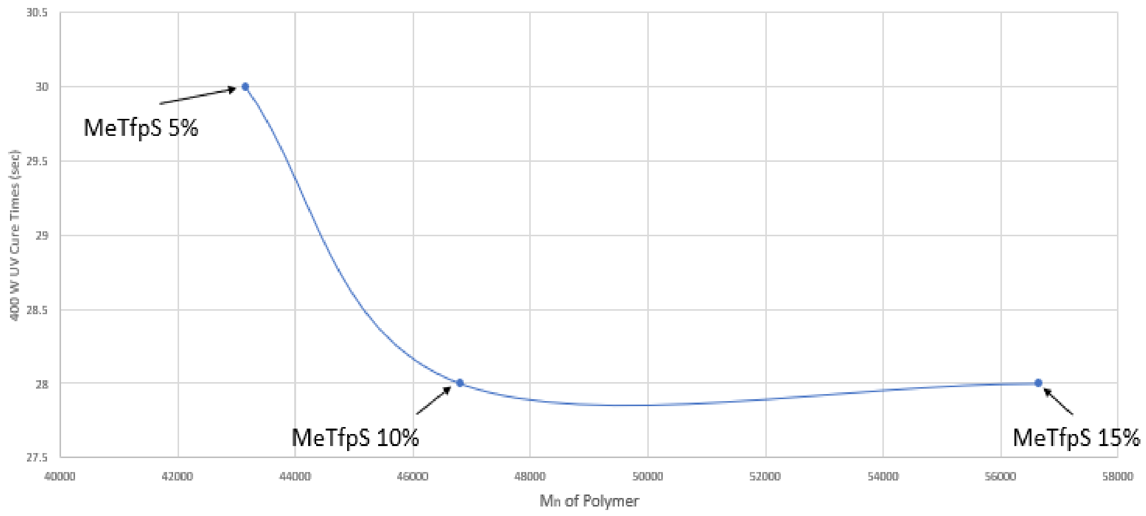


Figure 2.22: Dependence of the UV-Activated Cure Times of pastes of DP = 600 MeTfpS-Containing Terpolysiloxanes on the Polymer Molecular Weight for Varying mol % of MeTfpS Contents

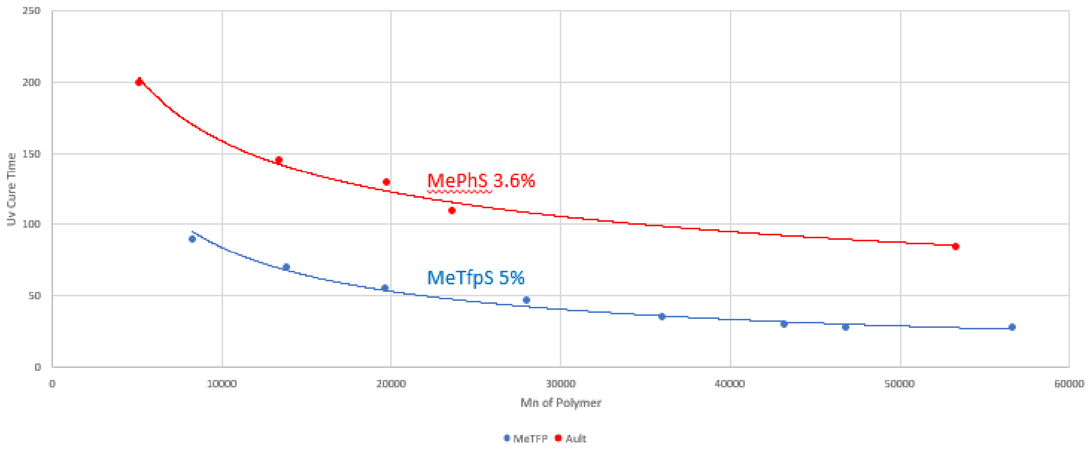


Figure 2.23: UV-Activated Cure Times: Comparison Between the Corresponding Pastes Prepared from $MePhS_{3.6}$- and $MeTfpS_5$-Containing Terpolysiloxanes

2.6 Mechanical Properties of Crosslinked Elastomers

In order to better understand the mechanical properties of MeTfpS-based terpolysiloxane elastomers and to compare their behavior with the previously studied

MePhS-containing counterparts,[17] DMA analyses were performed on all elastomers from prepared MeTfpS-containing terpolymers, and the results obtained are shown in Figures 2.24 and 2.25. It can be seen from Figure 2.24 that in the 5 mol % MeTfpS-containing terpolymer series the higher molecular weight terpolymer films (DP 240-600) exhibited “bumps” in both the storage and loss moduli in the -80 °C to -40 °C temperature range, indicative of strain-induced crystallization (SIC) consistent with the PDMS crystallization/melting in the temperature range from -50 °C to -40 °C. This is in stark contrast to the DSC data (see Figure 2.3) which exhibiting no crystallinity in these terpolysiloxanes in an unstressed state, indicating that mechanical strain placed onto the DMA-tested samples was the cause of the observed behavior in these higher molecular weight terpolymers. SIC in polysiloxane networks containing dimethyl and methylphenyl derivatives have been reported before, [17] as showing similar “bumps” in the same temperature range. With all tested terpolymers demonstrating almost identical gel content in networks (i.e., extent of crosslinking; See table 2.4) this clearly indicates that there is some critical length of network chains that is required for the formation of crystalline domains during the application of mechanical stress. Based on the data obtained in this work, this critical network chain length for these elastomers lies between the DPs of 160 and 240 (see Figure 2.25), consistent with what was recently discovered for their MePhS-containing counterparts. [17]

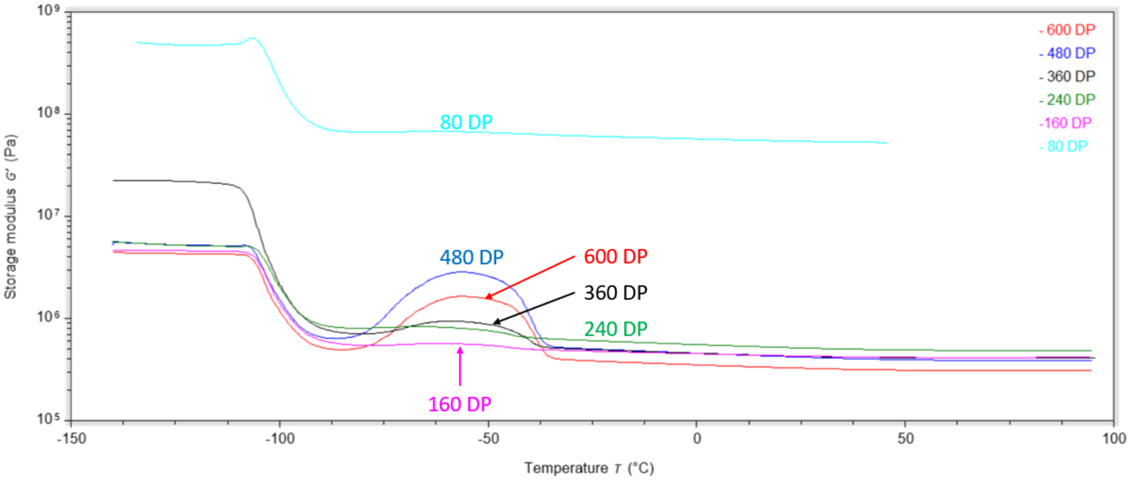


Figure 2.24: Storage Moduli of Elastomers from A-1/Ps Prepared from 5 mol % MeTfpS-Containing Terpolysiloxanes with Varying DPs.

In contrast to the above, in the varying MeTfpS content series only the sample containing 5 mol % (from Polymer A) exhibited the SIC "bump" within the temperature ranges from -80 to -40 °C. This indicates that there is also a critical MeTfpS % content between 5 and 10 mol % in these terpolysiloxanes that is responsible for preventing the SIC when mechanical strain is applied (see Figure 2.25).

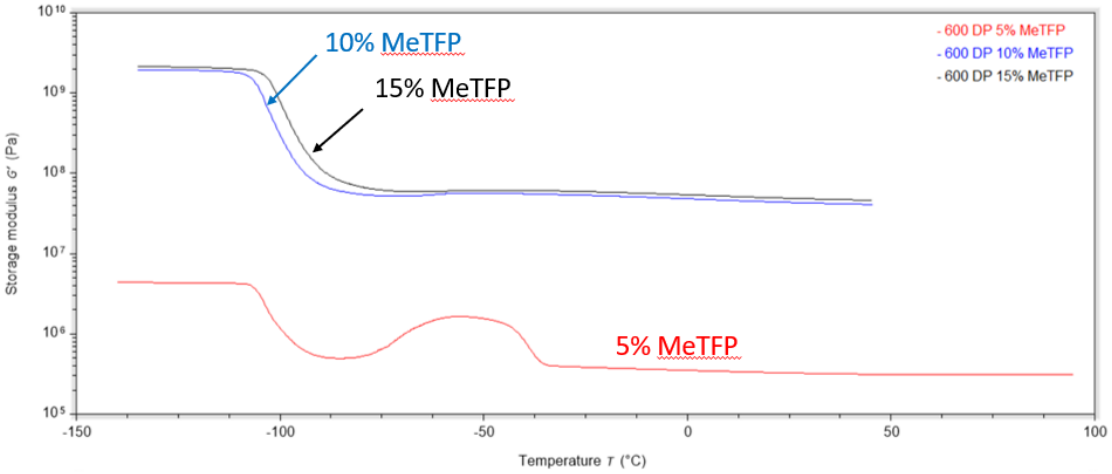
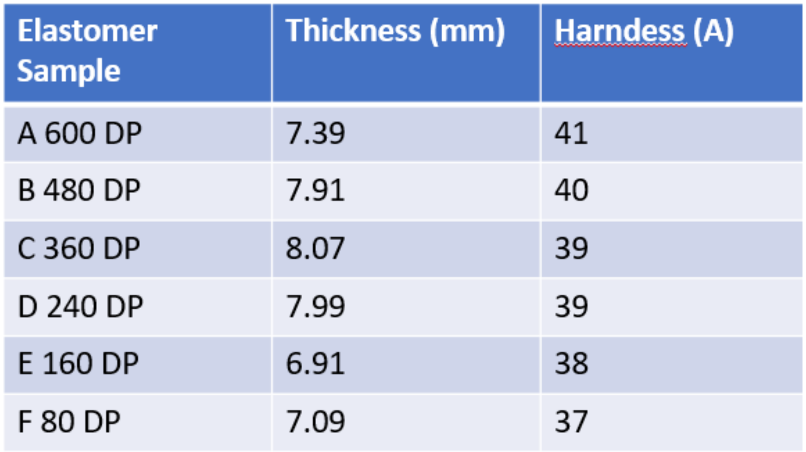


Figure 2.25: Storage Moduli of Elastomers from A-1/Ps Prepared from DP = 600 MeTfpS-Containing Terpolysiloxanes with Varying MeTfpS Content.

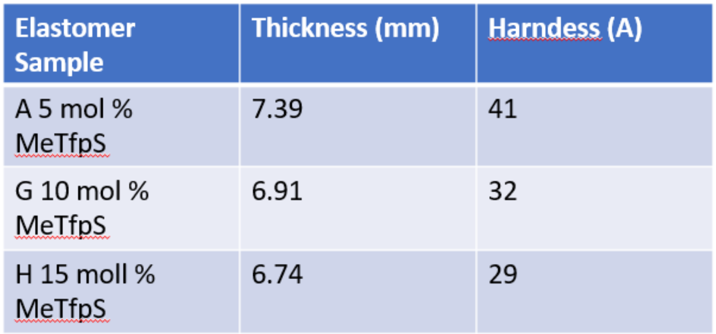
Hardness tests were also performed on the produced elastomers to observe effects of varying degrees of polymerization and mol % of MeTfpS on the system. The results obtained showed that as the DP decreased in the MeTfpS-containing elastomers (from 600 to 80) the hardness steadily decreased as well from 41 to 37 A, respectively. It was also observed that as the MeTfpS mol % was increased the overall hardness decreased with 5 mol % MeTfpS elastomers having the highest hardness at 41 A and 15 mol % counterparts having a harness of 29 A. This indicated that the hardness is reliant on both the DP and MeTfpS mol % used in the A/1P.

Table 2.5: Hardness values for Elastomers from A-1/Ps Prepared from 5 mol % MeTfpS-Containing Terpolysiloxanes with Varying DPs



Elastomer Sample	Thickness (mm)	Harndess (A)
A 600 DP	7.39	41
B 480 DP	7.91	40
C 360 DP	8.07	39
D 240 DP	7.99	39
E 160 DP	6.91	38
F 80 DP	7.09	37

Table 2.6: Hardness values for Elastomers from A-1/Ps Prepared from DP = 600 MeTfpS-Containing Terpolysiloxanes with Varying MeTfpS Content



Elastomer Sample	Thickness (mm)	Harndess (A)
A 5 mol % MeTfpS	7.39	41
G 10 mol % MeTfpS	6.91	32
H 15 moll % MeTfpS	6.74	29

CHAPTER III

CONCLUSION

3.1 Project Goals

The overall goal of this work was three-fold: (1) to prepare and evaluate a new class of fluorosilicone terpolymers for use in AM “inks”; (2) to compare the syntheses and properties of the obtained polymers with those synthesized and evaluated in Dvornic group before (those containing DiPhS, DiEtS and MePhS crystallization disrupting units),[5,17,18,19,20,21] with special emphasis on the mechanical properties; and (3) to determine if strain induced crystallization (SIC) appears in MeTfpS terpolymer-based films, as was recently discovered in their MePhS counterparts.[17]

To achieve these goals a synthetic strategy involving closely monitored (in real time) A-ROP with equilibration was used to prepare two series of MeTfpS-containing terpolysiloxanes with fixed DP and MeTfpS content, respectively, and their relevant properties were evaluated. All prepared polymers underwent structural, thermal, and mechanical property characterization by size exclusion chromatography (SEC), iodine value determination (IV), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and rheology testing (both steady and oscillatory shear performed on the compounded silicon pastes). Furthermore, *“all-in-one”* pastes (A-1/P) for application in direct ink write (DIW) additive manufacturing (AM) technique were prepared from all base polymers and then used in crosslinking studies to form elastomers (via UV-activated hydrosilylation reaction in air at room temperature), from which films were made for dynamic mechanical analysis (DMA).

3.2 Conclusions

Two series of MeTfpS-containing terpolymers (one consisting of six polymers with constant MeTfpS content of 5 mol % and varying DPs from 80 to 600, and another consisting of three polymers with constant DP of 600 and varying MeTfpS content from 5 to 15 mol %) were successfully synthesized using a silanol-initiated A-ROP with equilibration synthetic approach.

All polymerization reactions were closely monitored in real time using SEC and TGA monitoring techniques and the results obtained were compared with those previously obtained for closely related all-Me, DiPhS-, MePhS- and DiEtS-containing counterparts. As expected, the syntheses of MeTfpS-containing polymers closely matched the courses of occurrence of the syntheses of all-Me, MePhS- and DiEtS-containing homologues.

All polymers were characterized for their structure by IV, SEC and MHS analyses, and for their properties by viscosity, DSC and TGA techniques. The polymers were found to closely match the targeted molecular weights and molecular weight distributions, Si-Vi content and molecular chain linearity, to be completely amorphous, and to exhibit thermal stability similar to unmodified PDMS.

Rheological properties of polymer non-crosslinkable compounds with thixotropic additive and filler were prepared from all synthesized polymers and evaluated for their rheological flow properties by steady and oscillatory shear rheology within the shear rate range from 0.01 to 10.00 1/sec then 10.00 to 0.01 1/sec, and shear stress range from 3.00 to 10,000 (Pa), respectively. It was found that flow behavior of all tested compounds remained stable and unchanged over a year in storage and that longevity did not depend significantly on either the polymer's DP or MeTfpS content.

Hydrosilylation-curable A-1/Ps were prepared from all polymers adding a UV-activated Me_3CpMe-Pt catalyst and a Si-H containing oligomeric crosslinker to the compounds containing thixotropic additive and filler, and the rates of their crosslinking and crosslinking efficiency under exposure to UV light in air at room temperature were determined. It was found that in all cases these reactions led to almost quantitative crosslinking (routinely above 95% gelation) and, as in the case of previously described MePhS-containing terpolymer A-1/Ps, the crosslinking rates increased with increasing polymer molecular weight, albeit only slightly (assuming a constant catalyst concentration). The latter observation would indicate somewhat higher catalyst turn over numbers (TON) attainable in these MeTfpS-containing networks.

Similar to the closely related MePhS-containing terpolymers reported earlier, the MeTfpS-containing variants having DPs of 240 and above exhibited SIC within the -50 to -40 ^{o}C temperature range when subjected to DMA. This was, however, found to be a polymer composition-dependent property which disappeared for polymers having 10 mol % MeTfpS units or higher.

Hardness of MeTfpS-containing terpolymers-based elastomers was dependent on the DP of the base polymer and on the relative amount of MeTfpS units incorporated. It decreased with the decrease of the former and the increase of the latter.

CHAPTER IV

EXPERIMENTAL METHODS

4.1 Materials

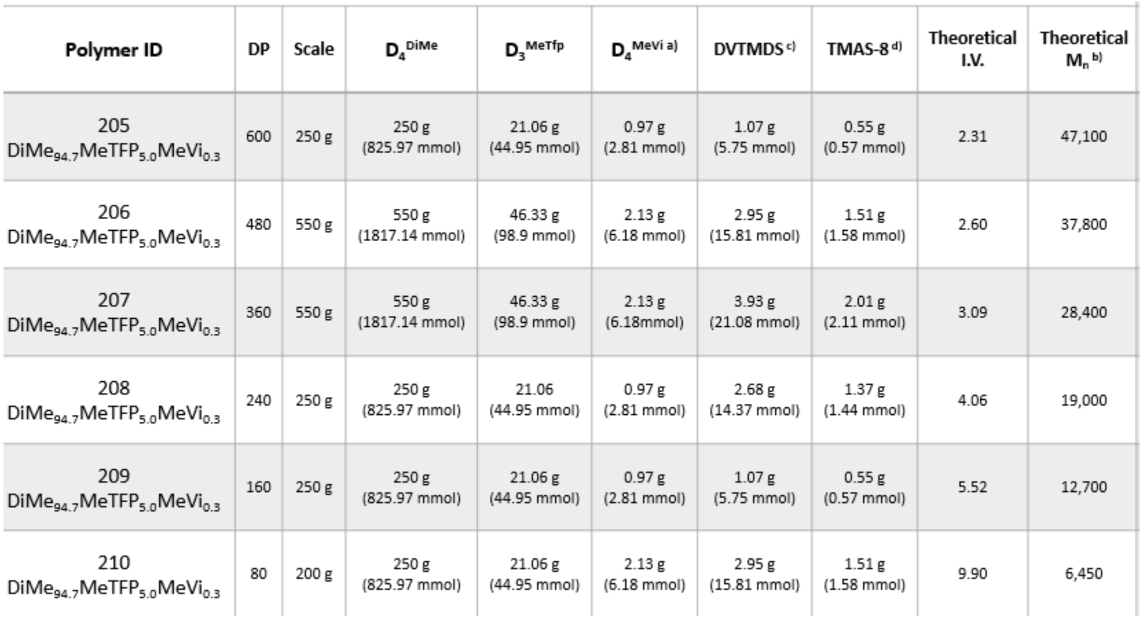
Octamethylcyclotetrasiloxane (D_4), 1,3,5-Tris[(3,3,3-triffluoropropyl)methyl]cyclotrisiloxane (D_3^{MeTfpS}), 1,3,5,7-tetramethyl-1,3,5,7-tetravinyl-cyclotetrasiloxane (D_4^{MeViS}) , 1,3-divinyltetramethyldisiloxane (DVTMDS), and oligomeric trimethylsilyl-terminated methyldrido-co-dimethylsiloxane crosslinker (HMS-151) were obtained from Gelest (Morrisville, PA) and used as received. Toluene, methylene chloride, methanol, and tetrahydofuran were purchased from Fisher Scientific (Pittsburg, PA). Bluesil Thixo Add 22646 thixotropic additive was obtained from Elkem Silicones (East Brunswick, NJ). Hexamethyldisilazane-treated (i.e., trimethylsilylated) AEROSIL R 812 S fumed silica filler was purchased from Evonik (Olmsted, OH); trimethyl(methylcyclopentadienyl)platinum(IV) (TMMCpPt) from Sigma-Aldrich (St. Louis, MO); and 1,3dioxolane (99.5%, stabilized) from Acros Organics (Pittsburg, PA). All commercial materials were used as received.

4.2 Methods

4.2.1 MeTfpS-Containg Terpolysiloxane Synthesis

All terpolymers were synthesized in a 500 mL three-necked round bottom flask equipped with a mechanical stirrer, nitrogen inlet and thermometer. Weighed amounts of D_4, D_3^{MeTfpS}, D_4^{MeViS}, and DVTMDS (see Table 4.1 and 4.2) were added into the flask and stirred while slowly heated to 100 °C. When 100 ^{o}C temperature was reached, the polymerization initiator, TMAS (m = 11; see Reaction Scheme 2.1) was dissolved into a 50 wt. % solution of THF and poured into the flask. The resulting reaction mixture was heated to 105-110 °C and left heated and mechanically stirred for 24 hrs. After 24 hrs, a nitrogen gas inlet and a condenser were attached to the reaction flask and the obtained reaction mixture was heated to 135 °C under nitrogen for another 2-4 hrs to decompose the initiator and stop the reaction. The resulting mixture was then heated to 175 °C to remove any remaining cyclics for yet another 2-5 hrs (under nitrogen purge), following which a low vacuum (water pump) was applied to the reaction flask and the distillation was continued for additional 12 hrs to complete this removal. Effectiveness of cyclics removal was monitored by TGA and SEC (See Figures 2.3 and 2.4).

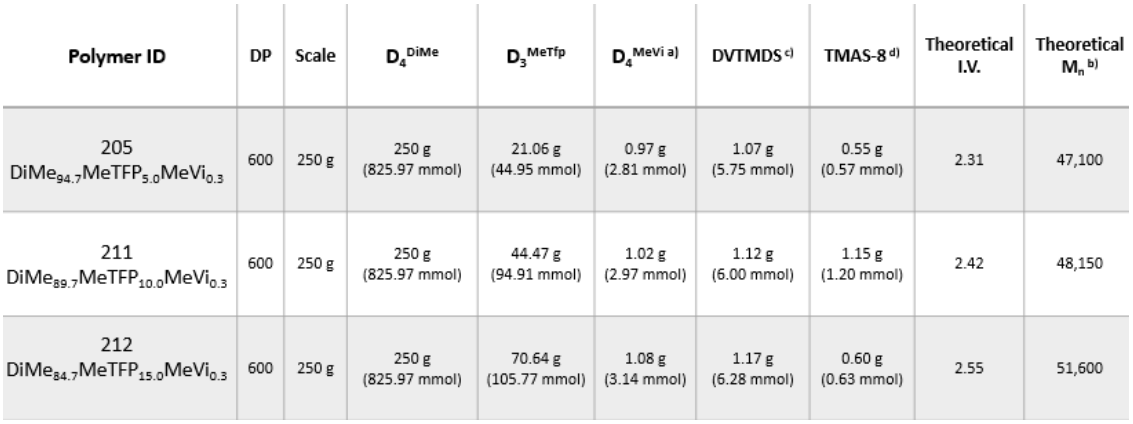
Table 4.1: Compositions of the Reaction Mixtures Used for the Syntheses of 5 mol % MeTfpS-Containing Terpolysiloxanes with Varying Degrees of Polymerization (DP)



Polymer ID	DP	Scale	D_4^{DiMe}	D_3^{MeTfp}	$D_4^{MeVi\ a)}$	DVTMDS [c)]	TMAS-8 [d)]	Theoretical I.V.	Theoretical M_n [b)]
205 $DiMe_{94.7}MeTFP_{5.0}MeVi_{0.3}$	600	250 g	250 g (825.97 mmol)	21.06 g (44.95 mmol)	0.97 g (2.81 mmol)	1.07 g (5.75 mmol)	0.55 g (0.57 mmol)	2.31	47,100
206 $DiMe_{94.7}MeTFP_{5.0}MeVi_{0.3}$	480	550 g	550 g (1817.14 mmol)	46.33 g (98.9 mmol)	2.13 g (6.18 mmol)	2.95 g (15.81 mmol)	1.51 g (1.58 mmol)	2.60	37,800
207 $DiMe_{94.7}MeTFP_{5.0}MeVi_{0.3}$	360	550 g	550 g (1817.14 mmol)	46.33 g (98.9 mmol)	2.13 g (6.18mmol)	3.93 g (21.08 mmol)	2.01 g (2.11 mmol)	3.09	28,400
208 $DiMe_{94.7}MeTFP_{5.0}MeVi_{0.3}$	240	250 g	250 g (825.97 mmol)	21.06 (44.95 mmol)	0.97 g (2.81 mmol)	2.68 g (14.37 mmol)	1.37 g (1.44 mmol)	4.06	19,000
209 $DiMe_{94.7}MeTFP_{5.0}MeVi_{0.3}$	160	250 g	250 g (825.97 mmol)	21.06 g (44.95 mmol)	0.97 g (2.81 mmol)	1.07 g (5.75 mmol)	0.55 g (0.57 mmol)	5.52	12,700
210 $DiMe_{94.7}MeTFP_{5.0}MeVi_{0.3}$	80	200 g	250 g (825.97 mmol)	21.06 g (44.95 mmol)	2.13 g (6.18 mmol)	2.95 g (15.81 mmol)	1.51 g (1.58 mmol)	9.90	6,450

[a]MeViS content in all terpolymers was 0.3 mol %. DiMeS content was 94.7 mol % in 5 mol % MeTfpS-Containing terpolymers. [b]M_t: targeted molecular weight; DP_t: targeted degree of polymerization. [c][DiViEB]: mmol DiViEB/mol (SiR_2O); SiR_2O: sum of all -SiR_2O- units introduced with cyclic monomers. [d][TMAS]: mmol silanolate/mol (SiR_2O))/2; SiR_2O: sum of all -SiR_2O- units introduced with cyclic monomers.

Table 4.2: Compositions of the Reaction Mixtures Used for the Syntheses of Terpolysiloxanes with Targeted DP of 600 and with 5, 10 and 15 mol % of MeTfpS Repeat Units



Polymer ID	DP	Scale	D_4^{DiMe}	D_3^{MeTfp}	$D_4^{MeVi\ a)}$	DVTMDS [c)]	TMAS-8 [d)]	Theoretical I.V.	Theoretical M_n [b)]
205 $DiMe_{94.7}MeTFP_{5.0}MeVi_{0.3}$	600	250 g	250 g (825.97 mmol)	21.06 g (44.95 mmol)	0.97 g (2.81 mmol)	1.07 g (5.75 mmol)	0.55 g (0.57 mmol)	2.31	47,100
211 $DiMe_{89.7}MeTFP_{10.0}MeVi_{0.3}$	600	250 g	250 g (825.97 mmol)	44.47 g (94.91 mmol)	1.02 g (2.97 mmol)	1.12 g (6.00 mmol)	1.15 g (1.20 mmol)	2.42	48,150
212 $DiMe_{84.7}MeTFP_{15.0}MeVi_{0.3}$	600	250 g	250 g (825.97 mmol)	70.64 g (105.77 mmol)	1.08 g (3.14 mmol)	1.17 g (6.28 mmol)	0.60 g (0.63 mmol)	2.55	51,600

[a]MeViS content in all terpolymers was 0.3 mol %. DiMeS content was 94.7 mol % in 5 mol % MeTfpS-Containing terpolymers, 89.7 mol % in 10 mol% MeTfpS-Containing terpolymers, and 84.7 mol % in 15 mol% MeTfpS-Containing terpolymers. [b]M_t: targeted

molecular weight; DP_t: targeted degree of polymerization. [c][DiViEB]: mmol DiViEB/mol (SiR_2O); SiR_2O: sum of all -SiR_2O- units introduced with cyclic monomers. [d][TMAS]: mmol silanolate/mol (SiR_2O))/2; SiR_2O: sum of all -SiR_2O- units introduced with cyclic monomers.

4.2.2 Monitoring of Polymerization Reactions

All MeTfpS-containing terpolysiloxane syntheses of this work were monitored by SEC and TGA. For these, samples of the reaction mixtures were withdrawn using a plastic pipet at 0-, 5-, 10-, 15-, and 30-minutes and then at 1-, 2-, 4-, and 24-hours of the reaction times. In addition, samples were also taken after each distillation (i.e., at 135 and 175 ^oC, and after 24-hour vacuum, respectively). All samples were kept in small glass vials until used in TGA and SEC.

4.2.3 Compounding of Silicon Pastes

All terpolymers were compounded into A-1/P pastes using a *FlackTek DAC 150.1 FV SpeedMixer*, a duel asymmetric centrifugal mixer, from FlackTek Inc. (Landrum, SC), as described previously.[5] The terpolymer base, catalyst, crosslinker, and thixotropic additive were added into a mixing cup, followed by trimethylsilylated AEROSIL R 812 S fumed silica filler in small portions, and mixed for 20 s at 3000 rpm to produce even mixtures. After all the filler had been added the pastes were mixed one final time for 1 min at 3000 rpm. The 80 g paste batches were compounded with filler in 15 wt. % of total sample weight.

4.2.4 UV-Activated Crosslinking (Curing) of Terpolysiloxane A-1/Ps

Samples used for crosslinking/curing experiments were prepared by mixing the base terpolymer and crosslinker in a [Si-Vi]/[Si-H] = 1:1 molar ration, as described previously.[5] The vinyl content of terpolymers was determined by iodometry (see Tables 2.1 and 2.2), while the hydride content of the HMS-151 crosslinker was accepted to be $f_{SiH} = 4$ (information provided by Gelest, Inc.). TMMCpPt catalyst was used as a UV-sensitive crosslinking catalyst.

Approximately 8-10 g of paste samples were cast into square films 100 mm x 100 mm x 0.5 mm in size and irradiated in a 400 W *SunRay 400 SM* UV flood lamp chamber (using UVA bulb optimized for 315-400 nm), irradiance at 3" – 115 mW cm^{-2} (Uvitron international, West Springfield, MA) at 10 s intervals until the films were completely crosslinked. Progression of crosslinking was monitored by pocking the surface of the film with a wooden Dynarex applicator sticks to observe the degree of tackiness. The cure time was deemed complete once the film exhibited no more tackiness and dimples formed from the prodding instantly dissipated. The final cure times were recorded. (See Figures 2.21 and 2.22).

4.2.5. Soxhlet Extraction

Soxhlet extraction was performed using a cellulose extraction thimble (25mm x 80mm), that was dried in a vacuum oven at 100 °C for two hours. Approximately 1.0 g of crosslinked film from the A/1Ps was cut into small pieces, weighed out and packed into the bottom of the thimble. A 500 mL round bottom flask was filled with approximately 300 mL of THF and 0.075 g of butylated hydroxytoluene (BHT), then stirred briefly to dissolve the BHT. The round-bottom flask was then fitted with the Soxhlet extractor containing the reaction thimble along with a condenser. Extraction was ran for 3-4 hours before the thimble was removed and airdried under the reaction hood overnight before being placed in a vacuum oven at 100 °C for two hours. sample were then weighed again. The difference in weight was recorded and the gel content of the samples were determined (see table 2.4).

4.3 Characterization Methods

4.3.1 Size Exclusion Chromatography (SEC)

SEC analyses were performed using a 1260 Infinity HPLC (Agilent Technologies) with Down Heleos-II (Wyatt Technology) light scattering, ViscoStar-II Viscometer (Wyatt Technology) viscometry, and a Optilab T-rEX (Wyatt Technology) refractive index detectors. All sample weights ranged from 0.2-0.29 mg of polymer dissolved into 10 mL of toluene and-were injected through a 0.2 μm syringe filter into the sample vials.

4.3.2 Thermogravimetric analysis (TGA)

TGA analyses was performed using a TA Instruments Thermogravimetric Analyzer, Model 550 (New Castle, Delaware, United States), under nitrogen purge (60 mL/min purge flow rate) at a heating ramp rate of 10 °C/min to 700 °C. Weights of the samples used ranged from 10-15 mg.

4.3.3 Differential scanning calorimetry (DSC)

DSC analyses was performed using a TA Instruments Differential Scanning Calorimeter, Model Q100 (New Castle, Delaware, United States). Aluminum pans purged with nitrogen gas (50 mL/min purge flow rate) and samples were first cooled and equilibrated to -80 °C, and then heated to 30 °C at a ramp rate of 10 °C/min. The responses of each sample were recorded by TA Universal Analysis software and TA Trios if applicable.

4.3.4 Dynamic mechanical analysis (DMA)

DMA tests were performed using a Q800 Dynamic Mechanical Analyzer (TA Instruments). 10 mm x 10 mm x 1.0 mm square sections were cut from the crosslinked films and placed in a shear sandwich clamp geometry for testing. All samples were tested at a constant frequency and amplitude of 1 Hz and 15 μm within the temperature range from -130 to 30°C. They were first thermally equilibrated for 5 min at -130°C and the heating rate was 5°C min^{-1}.

4.3.5 Rheology tests

Rheology tests were performed using an AR 2000ex Rotational Rheometer (TA Instruments) at 25 ˚C. Viscosities of terpolymers were determined in a constant shear stress mode (100 Pa) using cone/plate geometry (2˚, 40 mm diameter) with a 55μm truncation gap. Oscillatory shear tests were performed at constant frequency of 1 s^{-1}, with the stress sweep ranging from 3 to 10,000 Pa. Steady state shear tests were performed in two stages with reciprocal linear shear ramps, the first ranging from 0.01 to 10 S^{-1} and the second from 10 to 0.01 S^{-1}. 80 g paste samples were compounded from each base polymer for a year long shelf stability study evaluated by steady shear and oscillatory shear rheology tests. These pastes were first tested every week for one month, and since no significant rheological changes were observed during this time, the frequency of tests was changed to once a month for the remainder of the study.

4.3.6 Long-term shelf-life stability studies

80 g A-1/P samples were compounded and stored in an opaque plastic jar in a dark cooled environment (a fridge at about 40 ˚C). Their stability was then monitored by periodical testing using a metal spatula to stir the paste samples to test if viscosity has changed due to crosslinking. Samples were only removed and exposed to light during such rheological testing.

4.3.7 Mechanical characterization by determination of elastomers hardness

A Shore A Durometer was used to test the elastomers hardness. All UV-crosslinked elastomers were cut into 6-8 1cm x 1cm squares and stacked on top one another on a sturdy surface (lab bench) in order to meet the high level needed for the durometer (around 6.5 to 8mm). The durometer was then placed on the stack of elastomer squares and pushed down until the hardness was determined. All harnesses and thicknesses were recorded (See table 2.5 and 2.6).

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Functionalized Terpolysiloxanes on Their UV-Activated Crosslinking by Hydrosilylation and Mechanical Properties of Crosslinked Elastomers. Macromo. Rapid Commin. (2021)

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APPENDIX

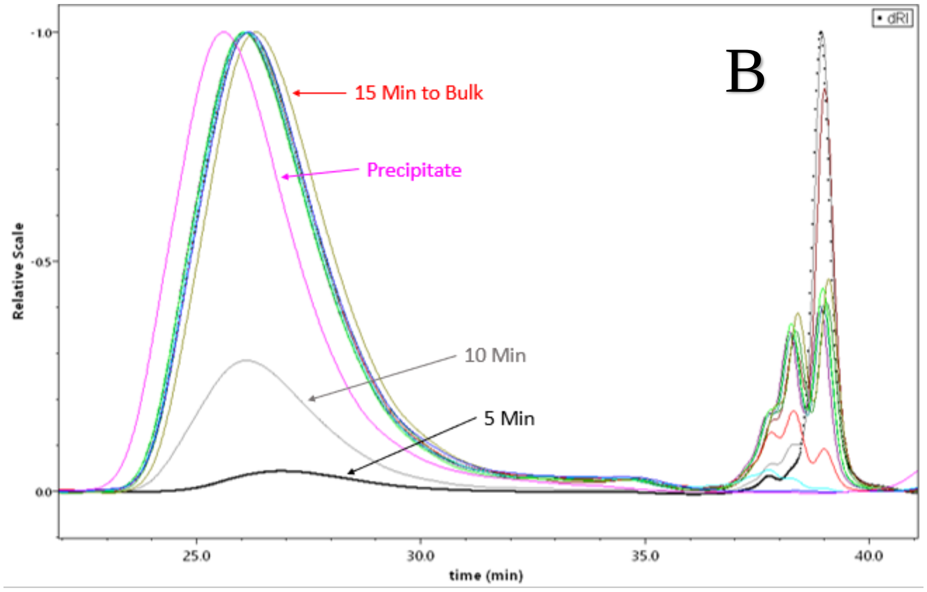

Figure 6.1: SEC Monitoring of the Synthesis of 5% MeTfpS-Containing Terpolysiloxane B Having Targeted DP of 480

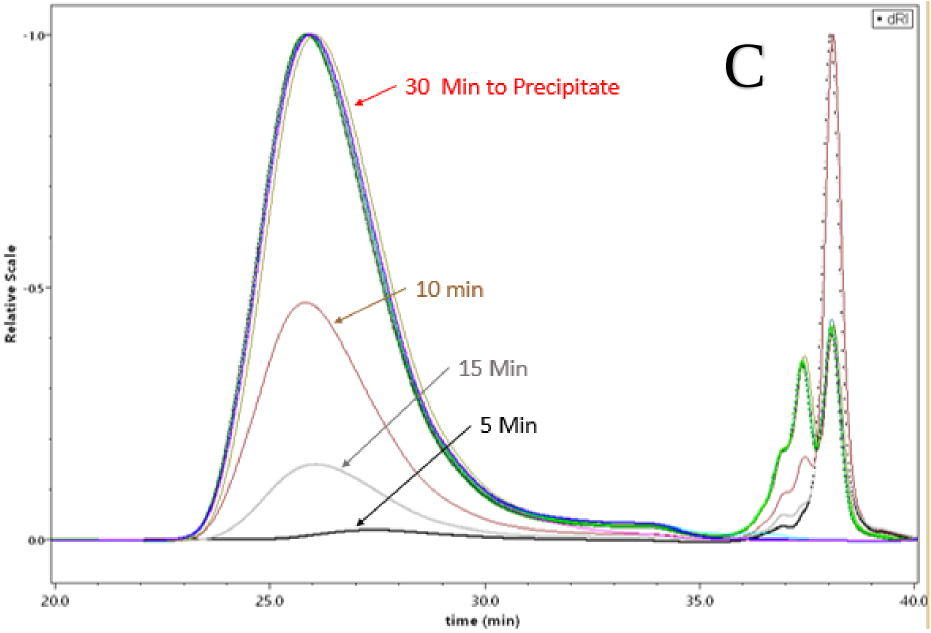

Figure 6.2: SEC Monitoring of the Synthesis of 5% MeTfpS-Containing Terpolysiloxane C Having Targeted DP of 360

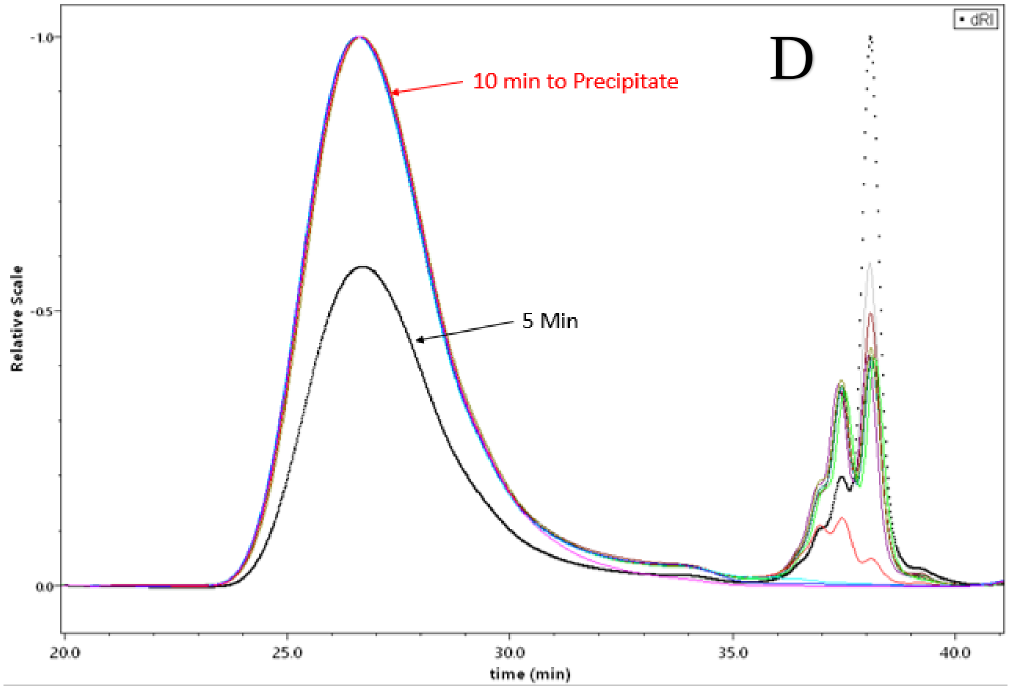

Figure 6.3: SEC Monitoring of the Synthesis of 5% MeTfpS-Containing Terpolysiloxane D Having Targeted DP of 240

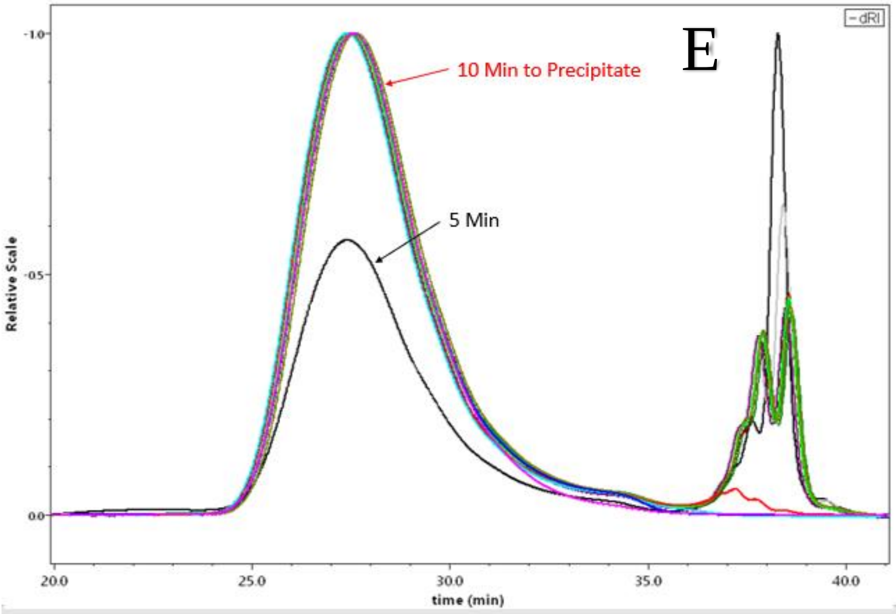

Figure 6.4: SEC Monitoring of the Synthesis of 5% MeTfpS-Containing Terpolysiloxane E Having Targeted DP of 160

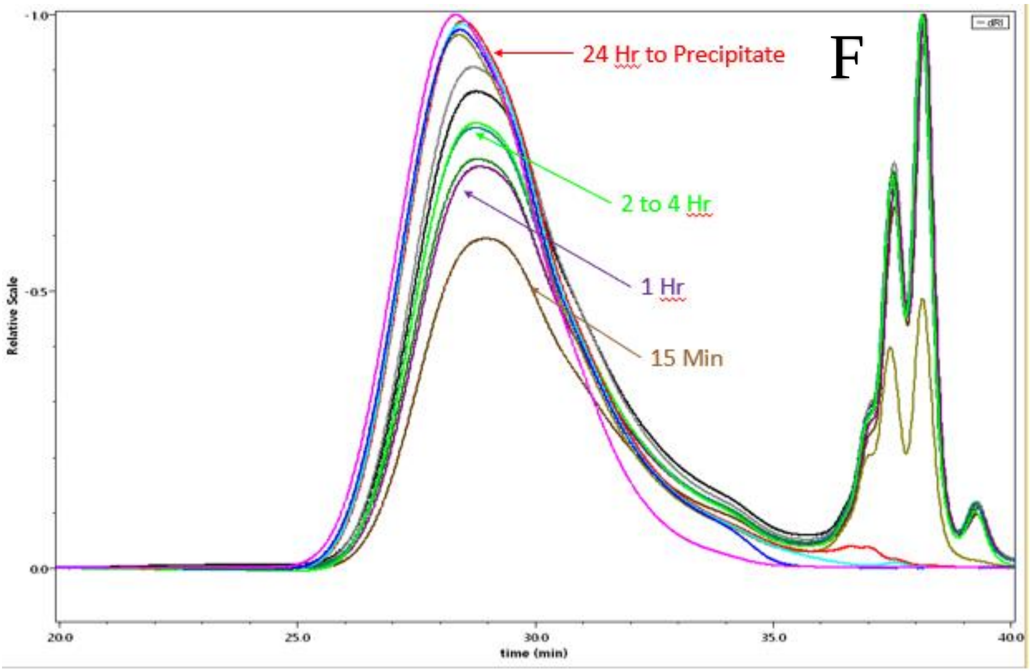

Figure 6.5: SEC Monitoring of the Synthesis of 5% MeTfpS-Containing Terpolysiloxane F Having Targeted DP of 80

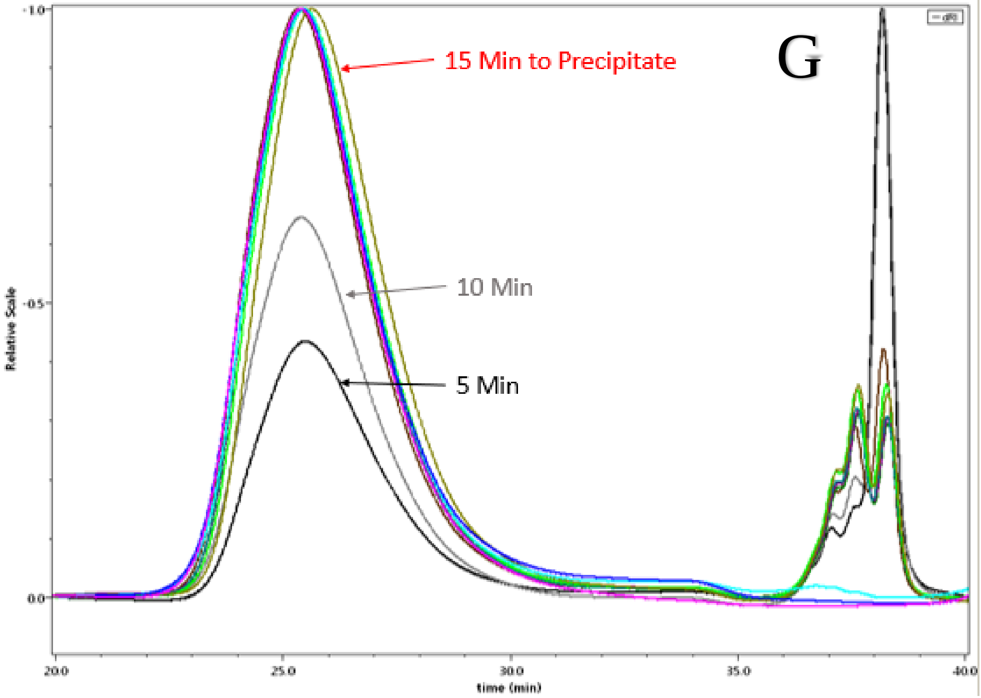

Figure 6.6: SEC Monitoring of the Synthesis of 10% MeTfpS-Containing Terpolysiloxane G Having Targeted DP of 600

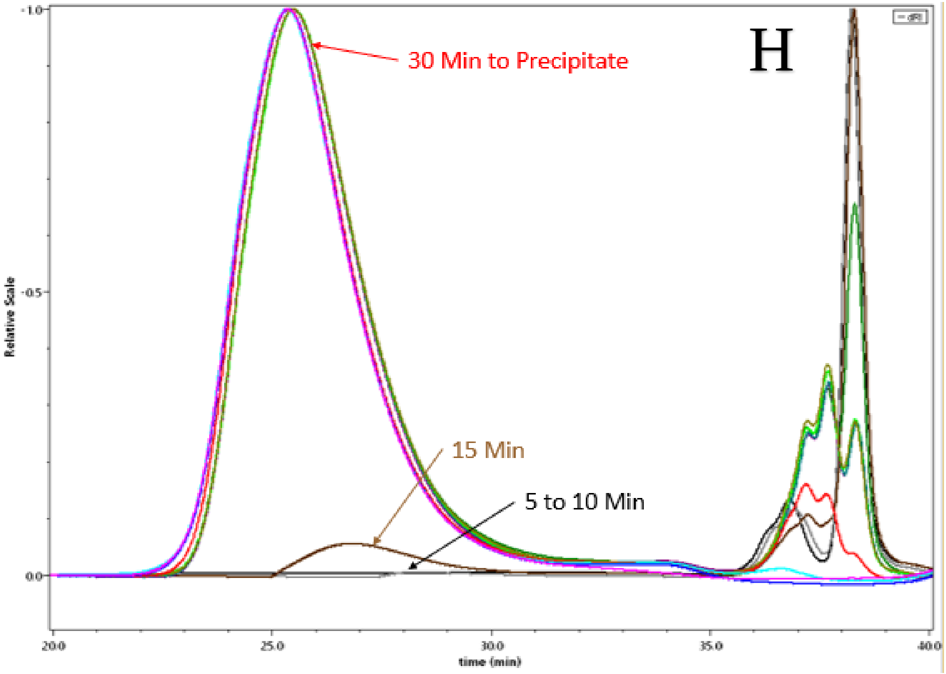

Figure 6.7: SEC Monitoring of the Synthesis of 15% MeTfpS-Containing Terpolysiloxane H Having Targeted DP of 600

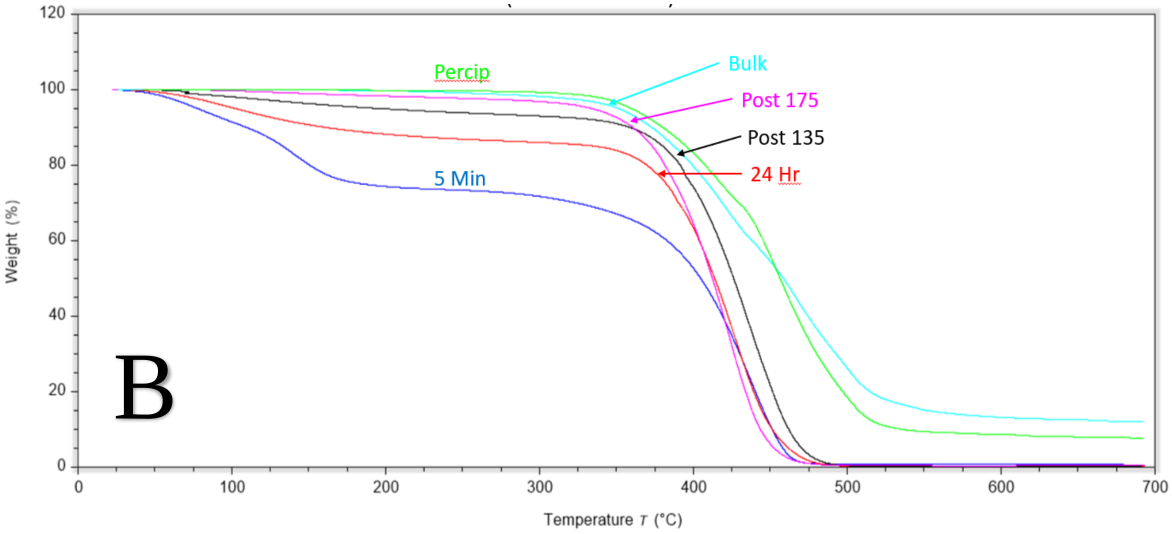

Figure 6.8: TGA Monitoring of the Synthesis of 5 mol % MeTfpS-Containing Terpolysiloxane B Having Targeted DP of 480

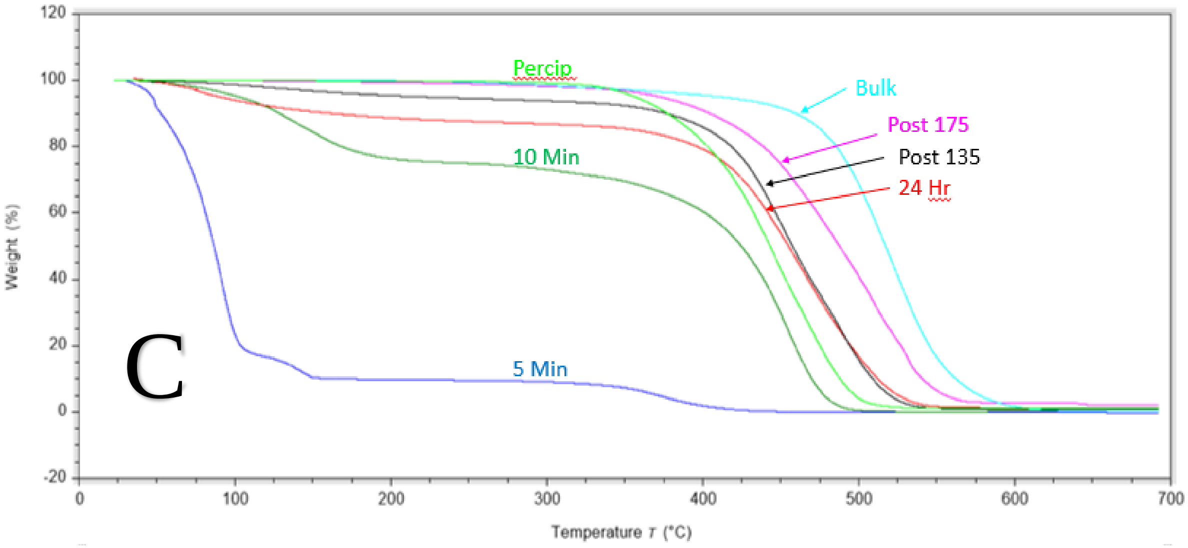

Figure 6.9: TGA Monitoring of the Synthesis of 5 mol % MeTfpS-Containing Terpolysiloxane C Having Targeted DP of 360

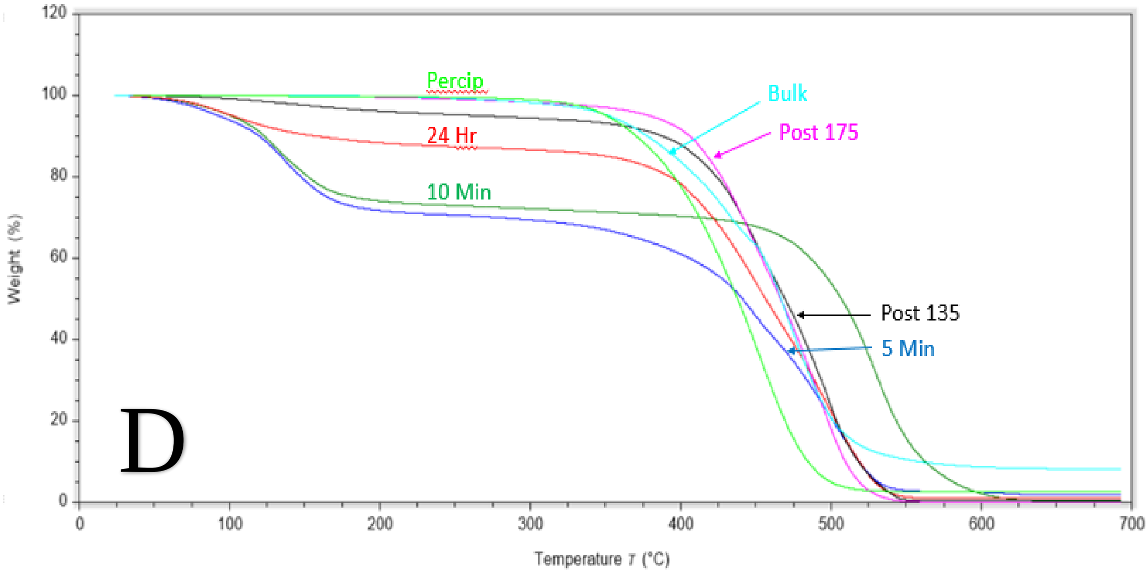

Figure 6.10: TGA Monitoring of the Synthesis of 5 mol % MeTfpS-Containing Terpolysiloxane D Having Targeted DP of 240

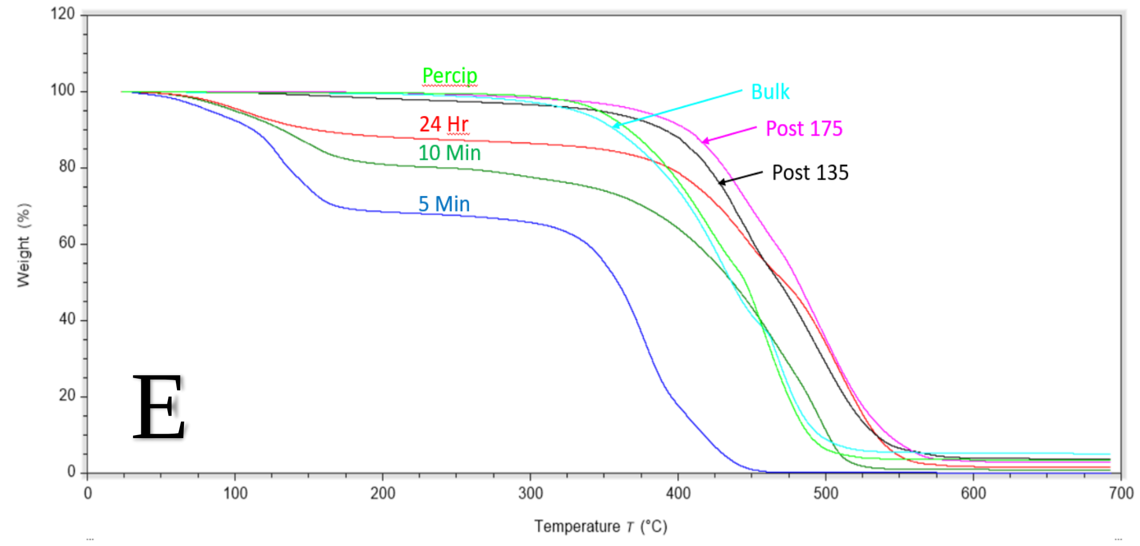

Figure 6.11: TGA Monitoring of the Synthesis of 5 mol % MeTfpS-Containing Terpolysiloxane E Having Targeted DP of 160

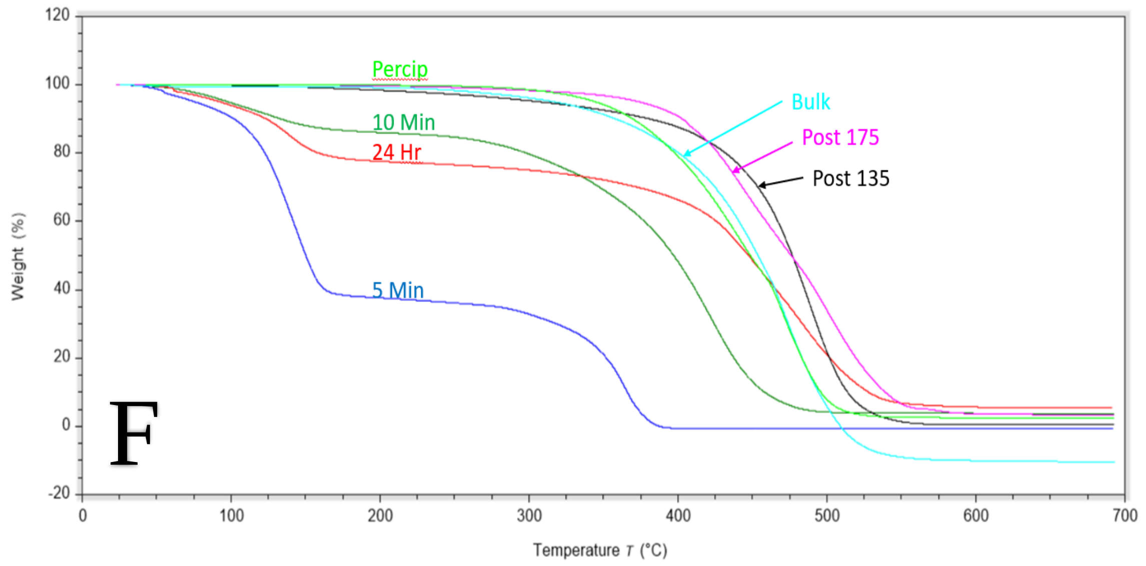

Figure 6.12: TGA Monitoring of the Synthesis of 5 mol % MeTfpS-Containing Terpolysiloxane F Having Targeted DP of 80

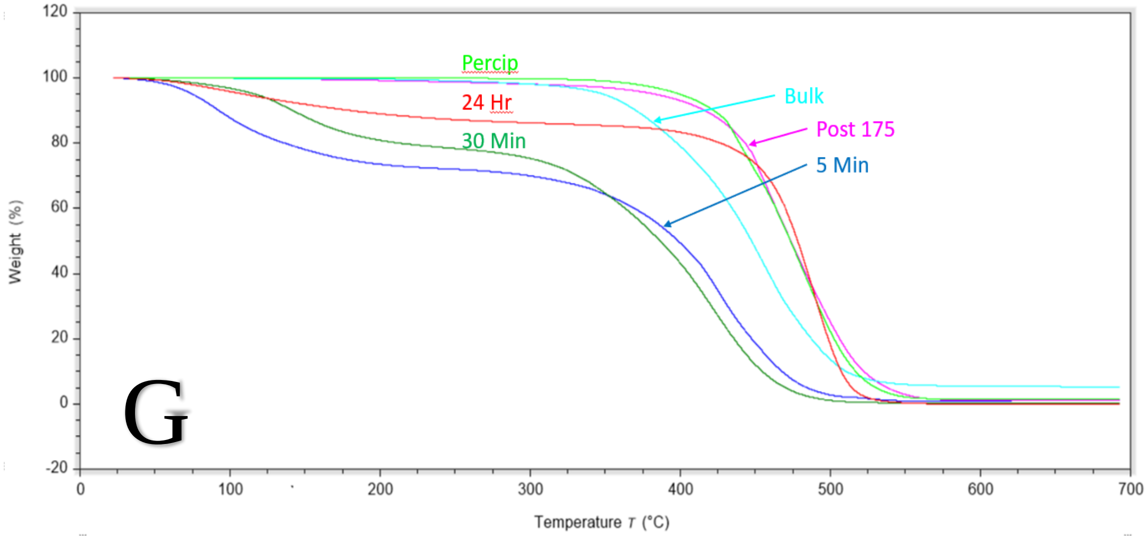

Figure 6.12: TGA Monitoring of the Synthesis of 10 mol % MeTfpS-Containing Terpolysiloxane G Having Targeted DP of 600

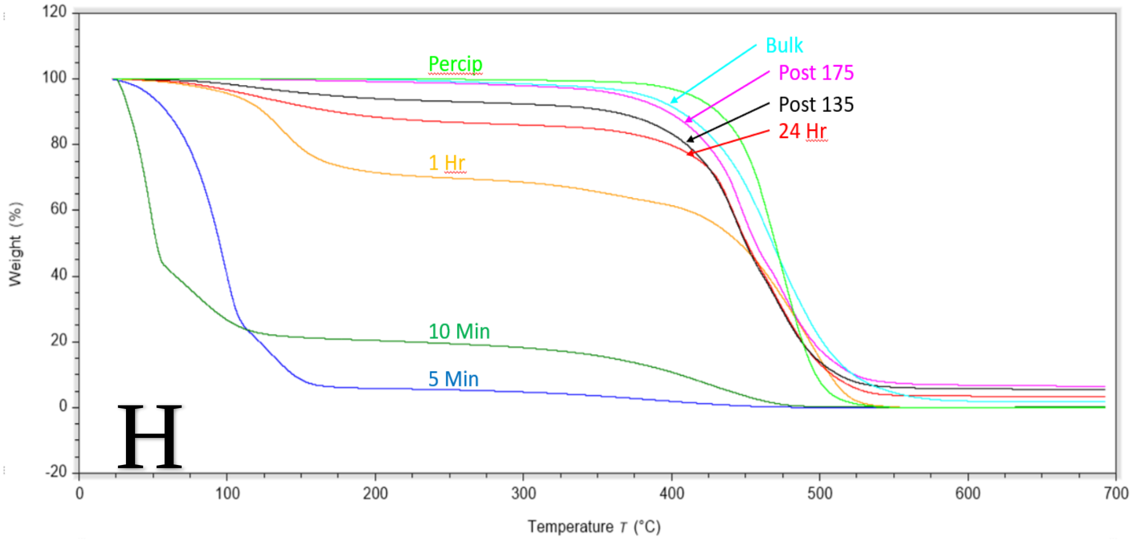

Figure 6.13: TGA Monitoring of the Synthesis of 15 mol % MeTfpS-Containing Terpolysiloxane H Having Targeted DP of 600

Figure 6.14: Oscillatory Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Week Two

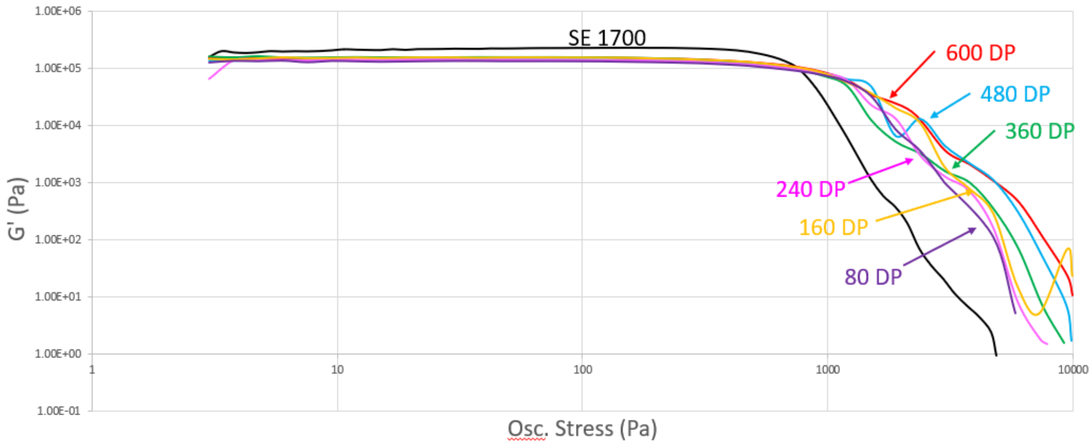

Figure 6.15: Oscillatory Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Week Three

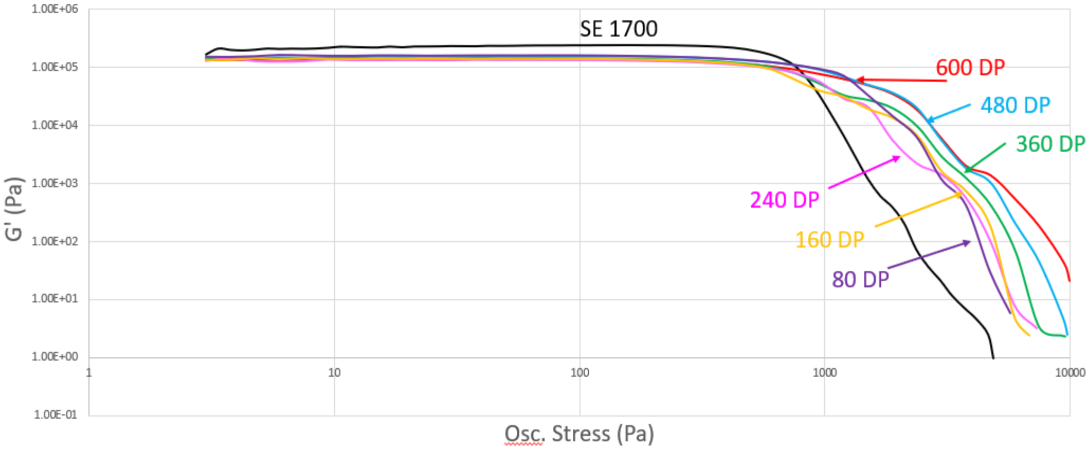

Figure 6.16: Oscillatory Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month One

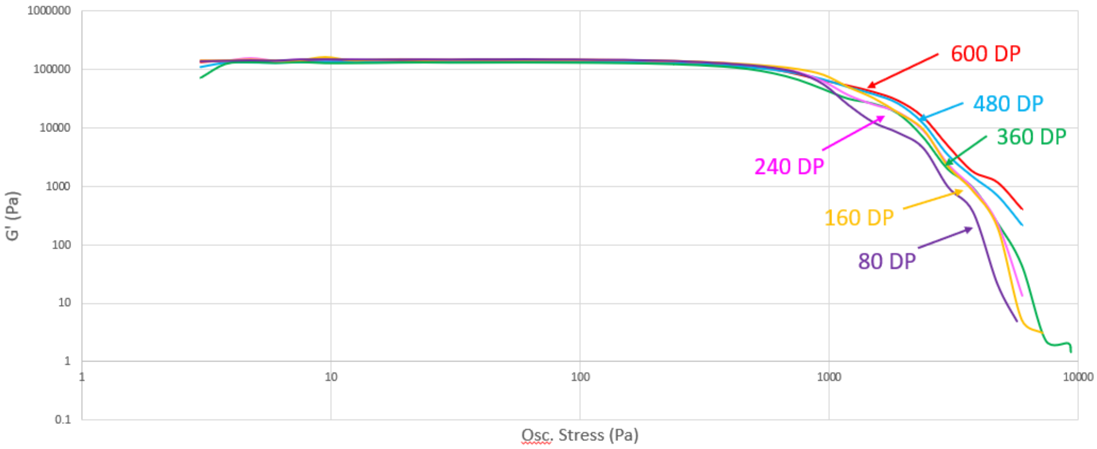

Figure 6.17: Oscillatory Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Two

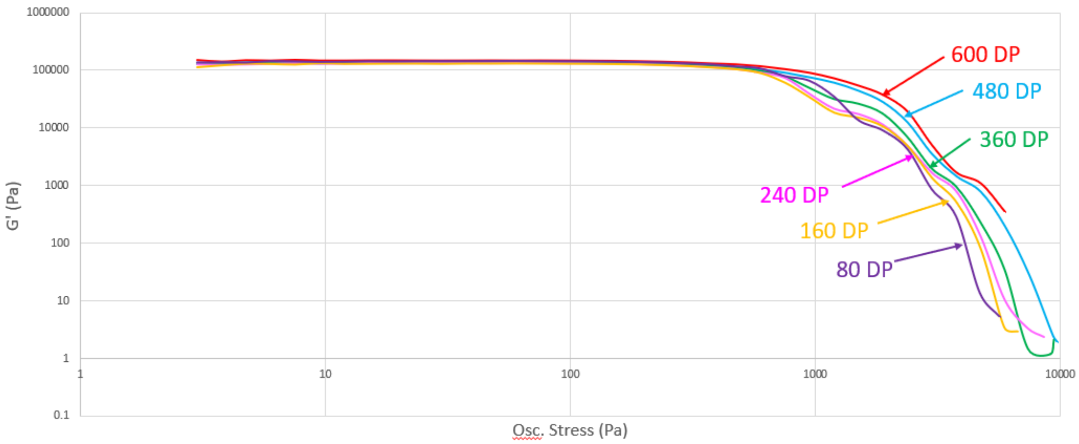

Figure 6.18: Oscillatory Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Three

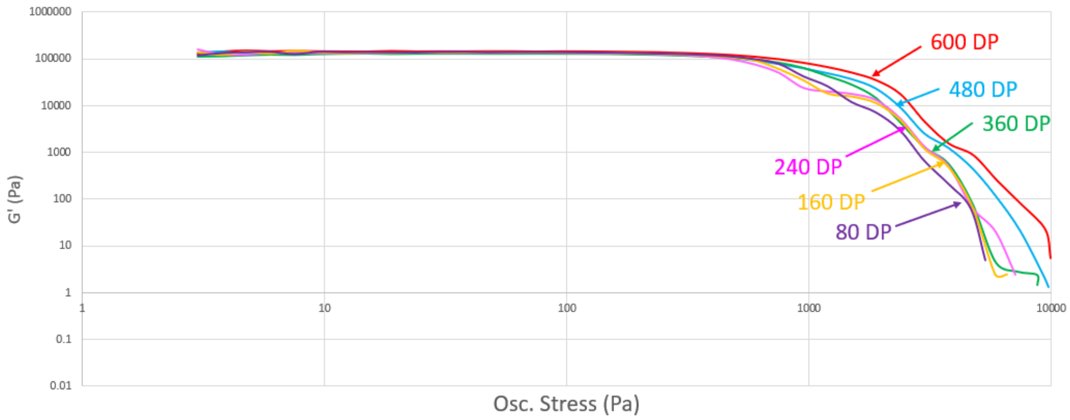

Figure 6.19: Oscillatory Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Four

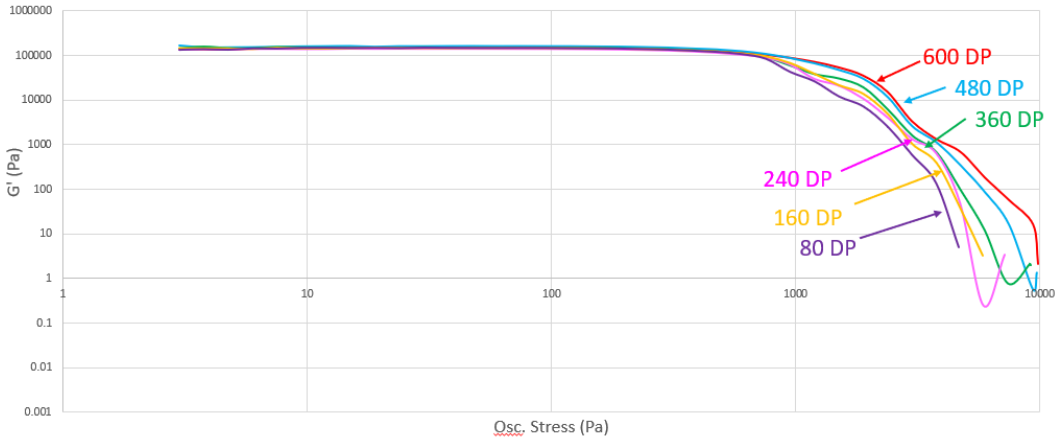

Figure 6.20: Oscillatory Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Five

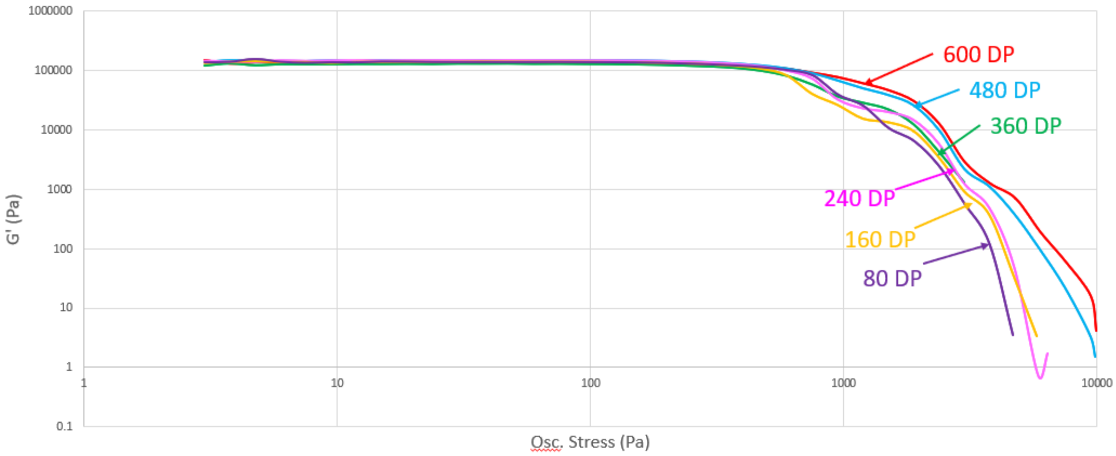

Figure 6.21: Oscillatory Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Six

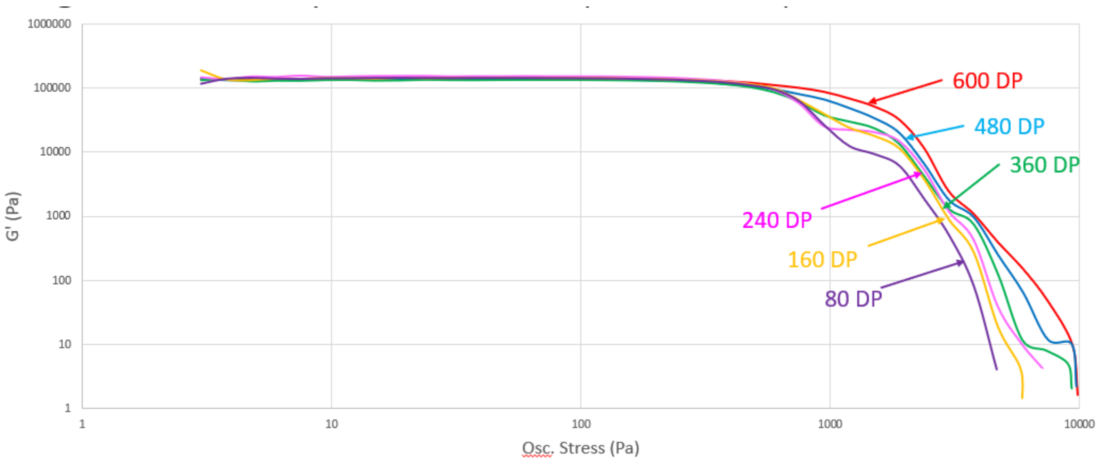

Figure 6.22: Oscillatory Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Seven

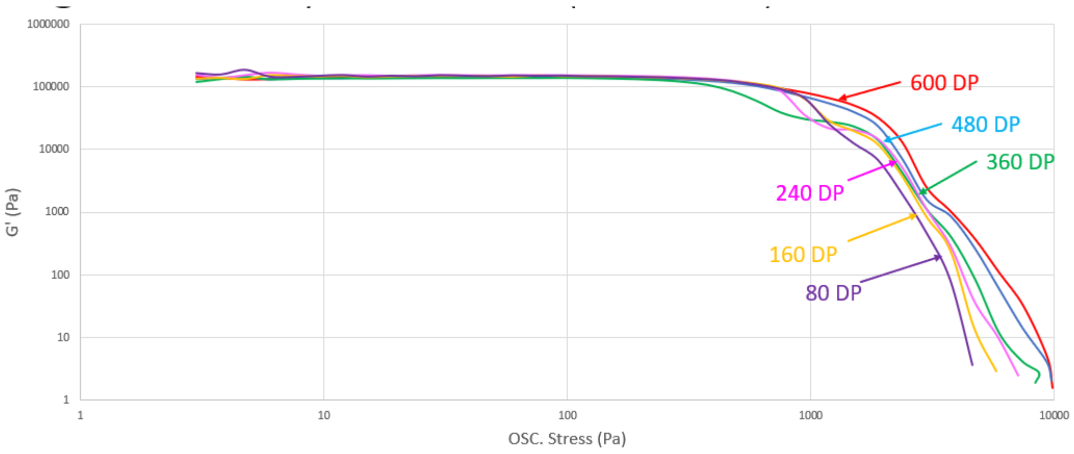

Figure 6.23: Oscillatory Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Eight

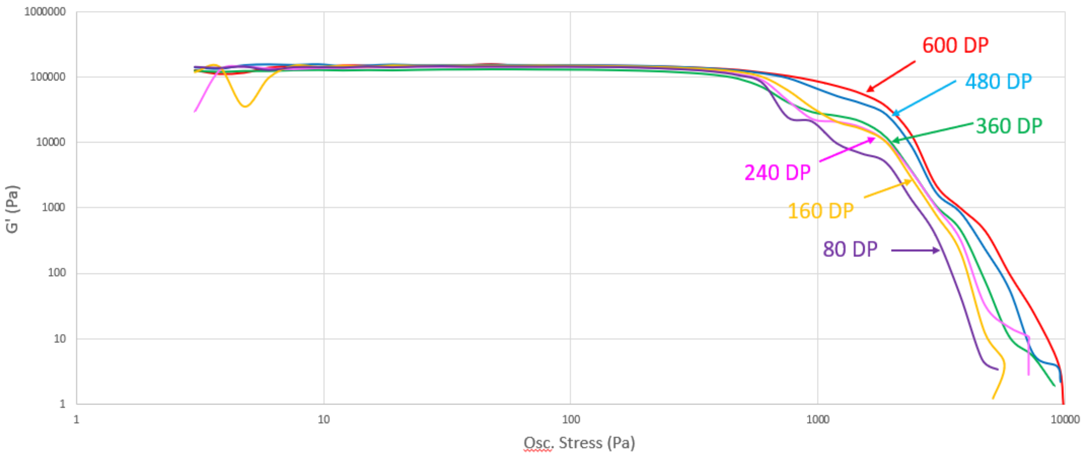

Figure 6.24: Oscillatory Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Nine

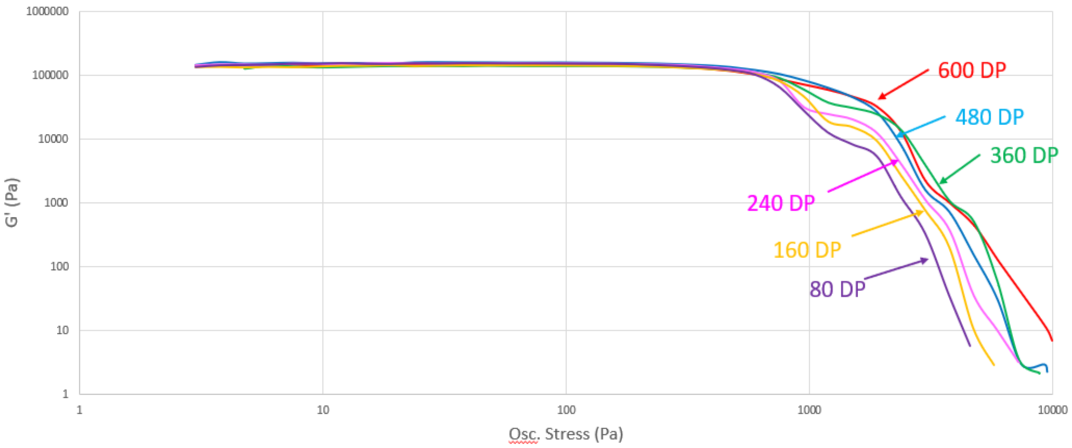

Figure 6.25: Oscillatory Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Ten

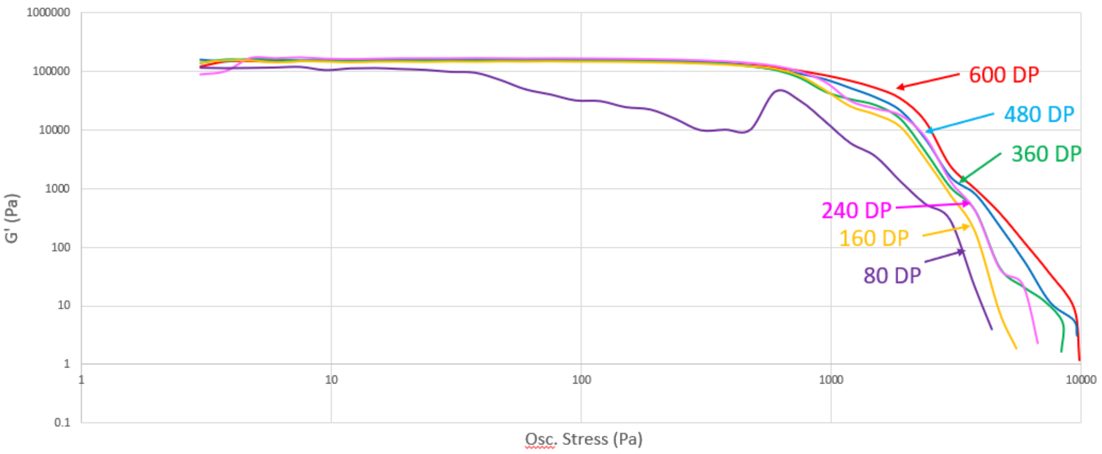

Figure 6.26: Oscillatory Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Eleven

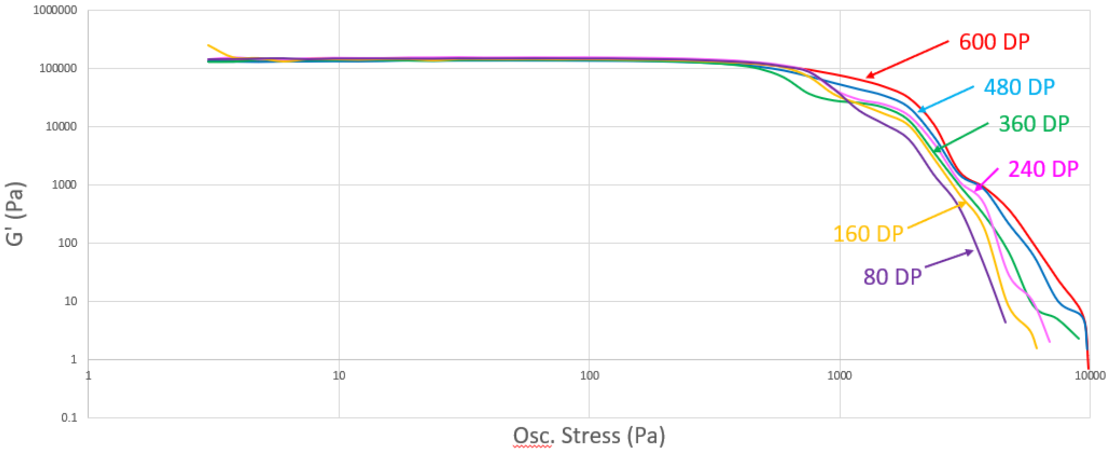

Figure 6.27: Oscillatory Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Twelve

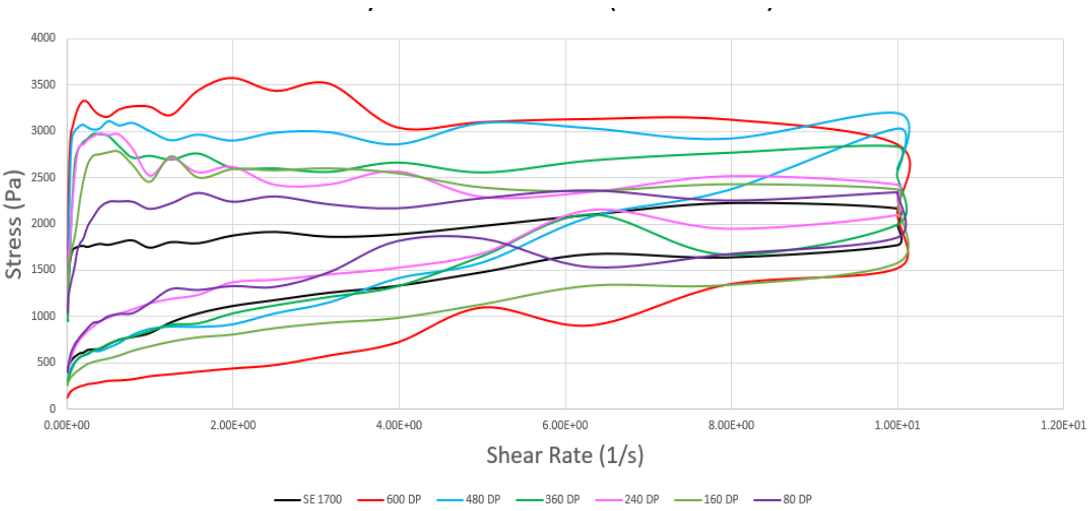

Figure 6.28: Steady Shear Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Week Two

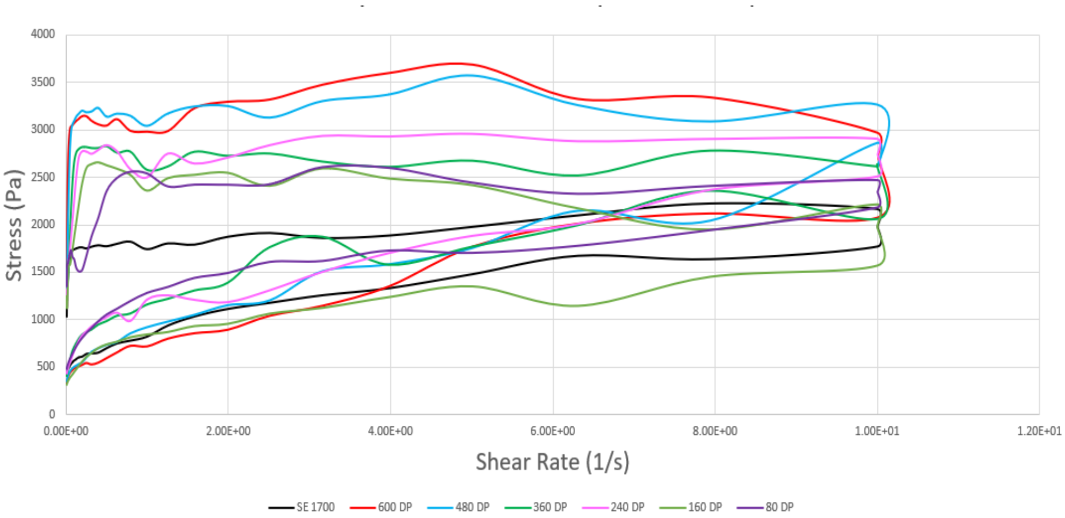

Figure 6.29: Steady Shear Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Week Three

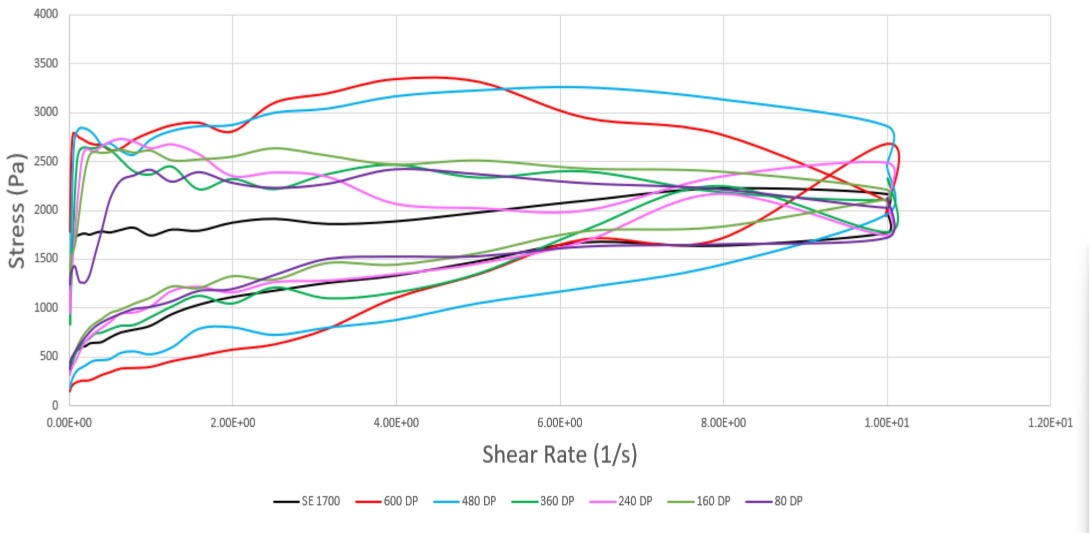

Figure 6.30: Steady Shear Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month One

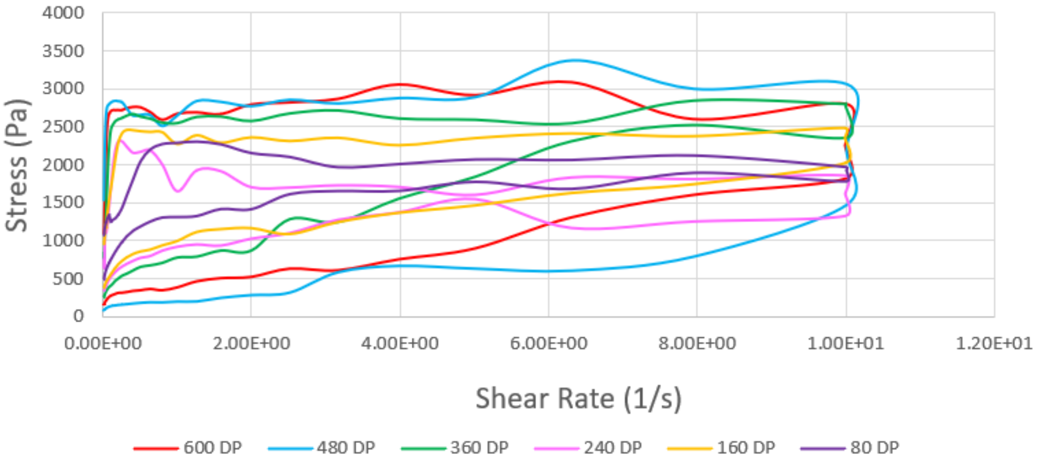

Figure 6.31: Steady Shear Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Two

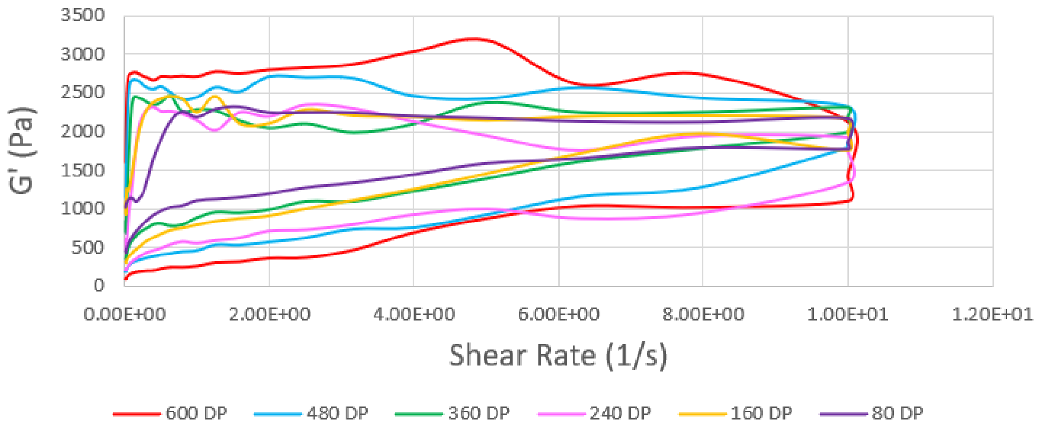

Figure 6.32: Steady Shear Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Three

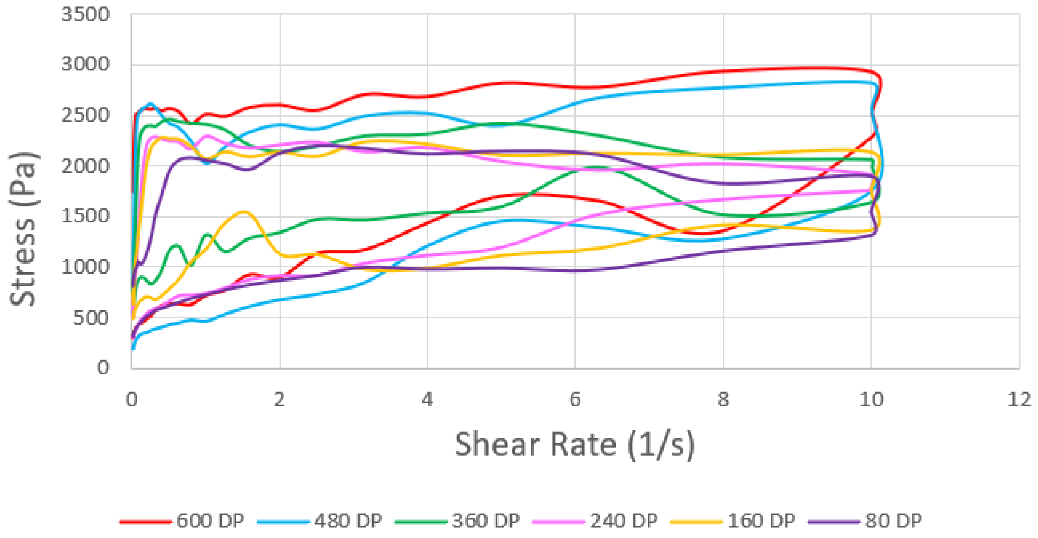

Figure 6.33: Steady Shear Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Four

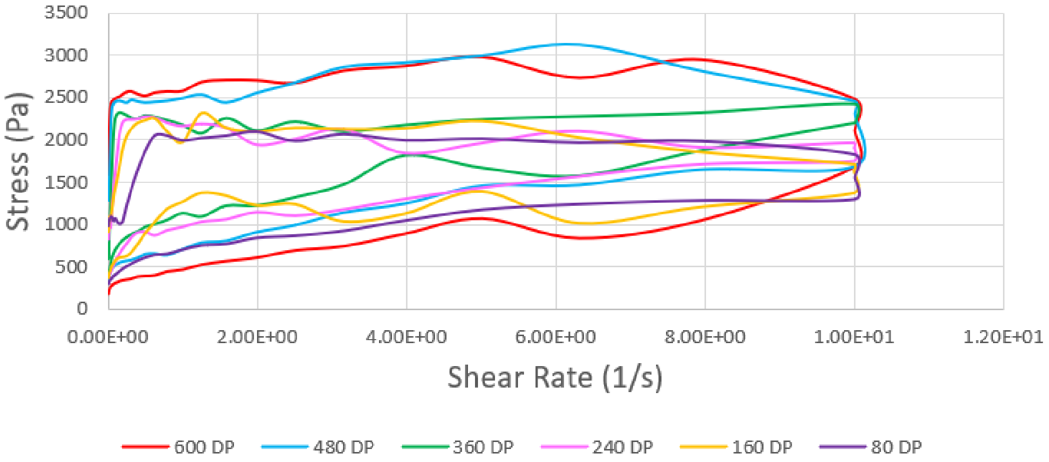

Figure 6.34: Steady Shear Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Five

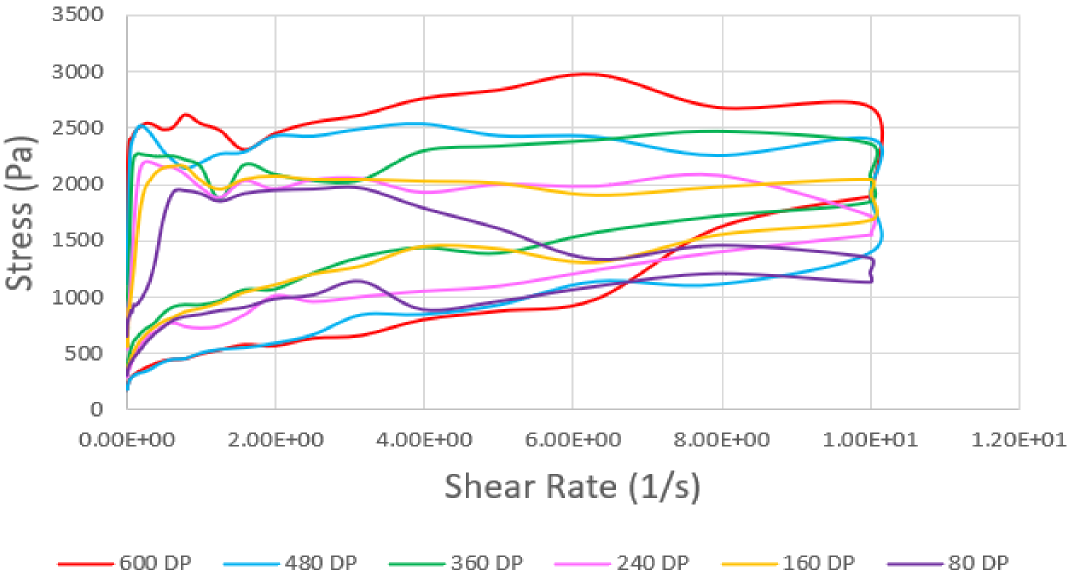

Figure 6.35: Steady Shear Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Six

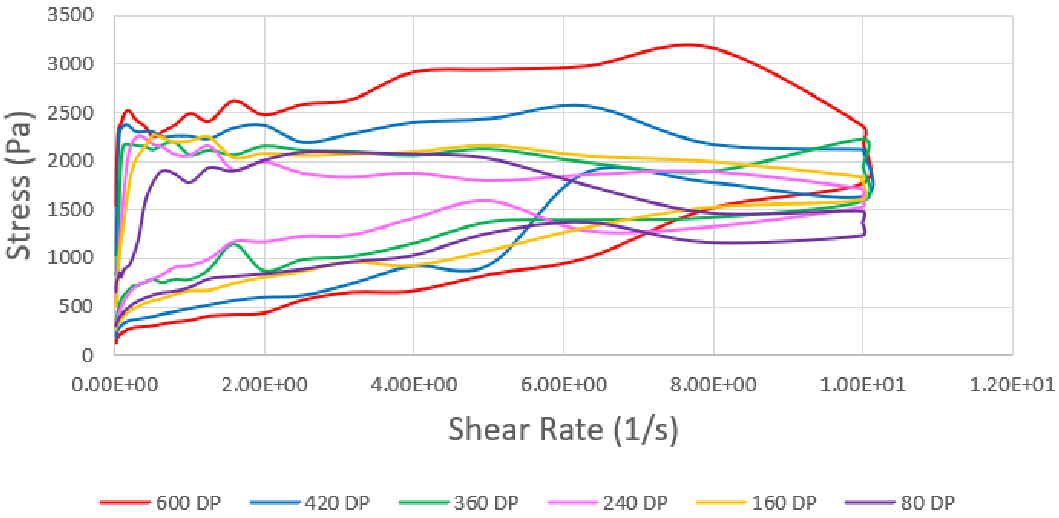

Figure 6.36: Steady Shear Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Seven

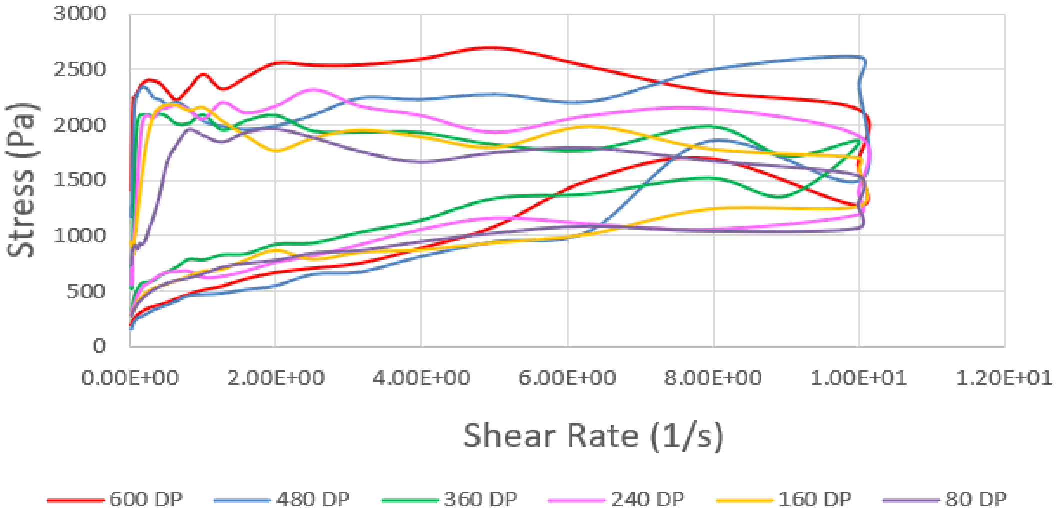

Figure 6.37: Steady Shear Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Eight

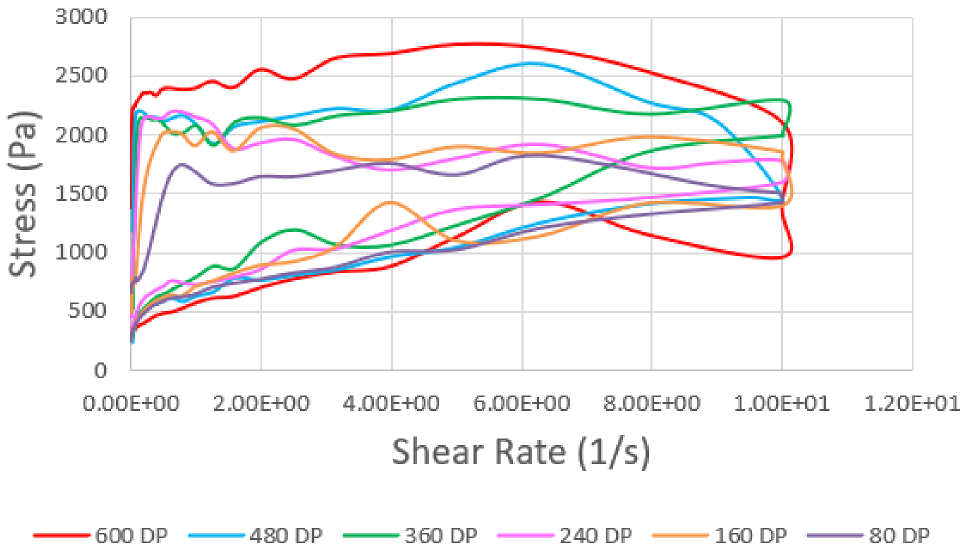

Figure 6.38: Steady Shear Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Nine

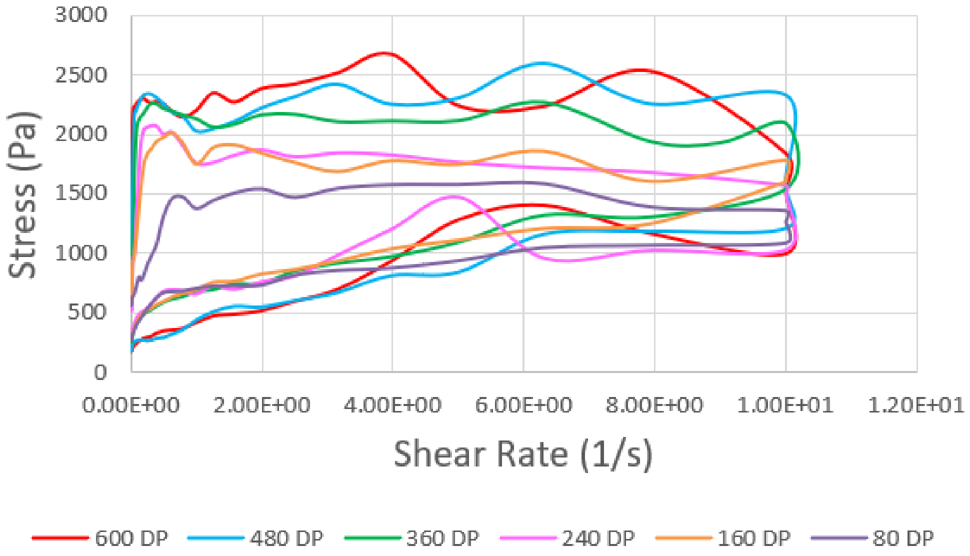

Figure 6.39: Steady Shear Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Ten

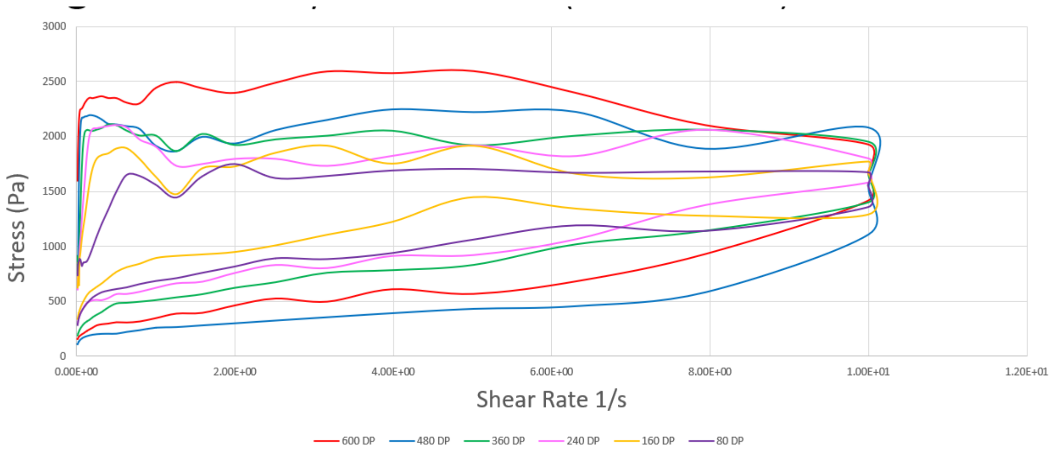

Figure 6.40: Steady Shear Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Eleven

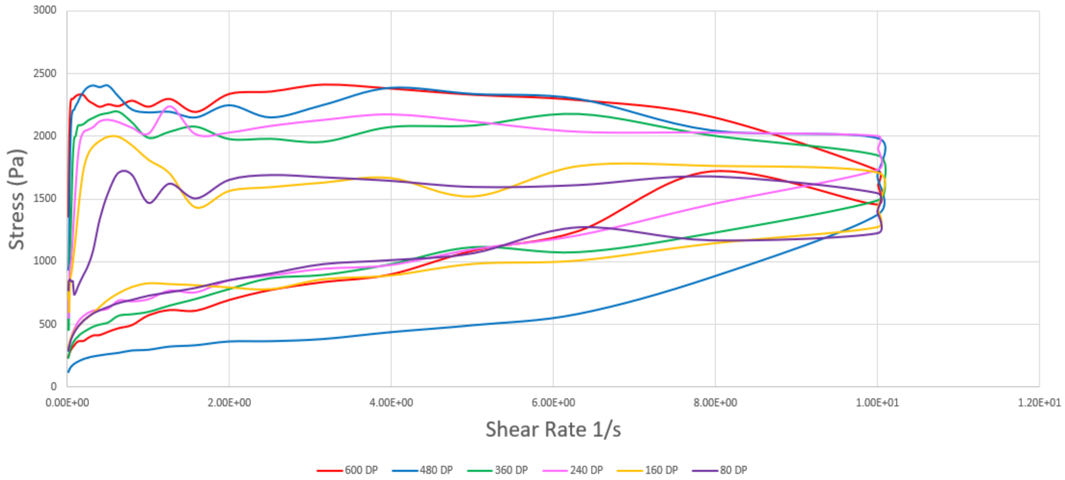

Figure 6.41: Steady Shear Rheology of 5% MeTfpS-Containing Terpolysiloxane Pastes with Varying Degrees of Polymerization from 80 to 600, Month Twelve