Novel Fluoro-Terpolymers for Coatings Applications

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Received October 26, 2004; Revised Manuscript Received April 7, 2005

ABSTRACT: A series of thermally stable, elastomeric and hydrophobic fluoro-terpolymers of tetrafluoroethylene (TFE), vinyl acetate (VAc), and poly(dimethylsiloxane) methyl acrylate-terminated (PDMSMA), P(TFE-ter-VAc-ter-PDMSMA), were synthesized in supercritical carbon dioxide. Because the differences in reactivity ratios of TFE and PDMSMA precluded copolymerization, VAc was introduced into the feed resulting in terpolymers with yields as high as 64%, weight-average molar masses between 29 and 173 kg mol^{-1}, and polydispersity between 1.8 and 3.7. DSC examination of the fluoro-terpolymers indicated a microphase separation consisting of P(TFE−VAc) and P(PDMSMA) domains for all terpolymer compositions. However, P(TFE-ter-VAc-ter-PDMSMA) terpolymers having TFE content greater than or equal to 55.2 mol % had additional semicrystalline domains, providing a T_g of −120 °C [P(PDMSMA) domains], a T_g of 28 °C [P(TFE−VAc) domains], and a T_m of 235 °C [PTFE domains]. Cross-linked terpolymers having 55.2 mol % of TFE lose only 5% of their mass after 14 days under continuous heating at 200 °C in air. As determined from stress/strain curves, the elastic modulus of the cross-linked terpolymer films increased with molar mass of the linear polymer, fluorocarbon composition, and curing time. According to dynamic advancing and receding water contact angle data, both un-cross-linked (112°/69°) and cross-linked (125°/81°) terpolymer films were more hydrophobic than TFE−VAc copolymer films (90°/65°). X-ray photoelectron spectroscopy revealed that both un-cross-linked and cross-linked films were surface-enriched with silicone (and not fluorine) at the air−polymer interface relative to bulk composition. These results suggest that PDMS pendant groups were oriented at the air surface, likely due to the combination of greater mobility and lower surface tension than $-CF_2-$ groups of TFE segments. These novel P(TFE-ter-VAc-ter-PDMSMA) terpolymers exhibit the properties associated with polysiloxanes and fluoropolymers, making them useful for coatings applications.

Introduction

Fluoropolymers are chemically resistant and thermally stable, polysiloxanes are thermally stable and elastomeric, and both are hydrophobic. In an attempt to create a polymer that combines the properties of both fluoropolymers and polysiloxanes, we sought to create a polymer that would be chemically and thermally stable, have very low surface energy, and be more elastomeric than commercial fluoropolymers.[1] Currently, fluorosilicones are used commercially as high-temperature lubricants and elastomers because of their excellent chemical, thermal, and thermooxidative resistance.[2,3] Cross-linked fluorosilicone polymers are also promising in applications that require lubricity and elasticity and may be useful as low surface energy and internal release coatings. [3−6]

The solubility of both fluorinated and organosiloxane polymers in supercritical carbon dioxide ($scCO_2$) makes the synthesis of fluorinated organosiloxanes particularly attractive from an environmentally friendly process perspective. CO_2 is an alternative to organic solvents traditionally used in applications such as separations,[7] extractions,[8] coatings,[9] and polymerizations.[10−18] Because $scCO_2$ has a critical pressure (P_c) of 73.8 bar and a critical temperature (T_c) of 31.1 °C,[19] it presents an interesting and easily accessible medium in which to manipulate solubility by simply varying the temperature and pressure of the system. While many nonionic, low molar mass organic molecules are soluble in $scCO_2$, only some polymers like fluoropolymers,[20,21] poly(siloxane)s,[22] and poly(ether−carbonate)s[23] exhibit significant solubility in CO_2. For example, we recently reported the synthesis and solubility of linear TFE−VAc copolymers in $scCO_2$[10,11,21] and found that high molar mass copolymers could be prepared which are soluble in $scCO_2$ for polymer compositions having less than 19 mol % TFE. Our goal was to build on this expertise to synthesize polymers that incorporated fluorocarbon and siloxane functional groups.

While fluorosilicone polymers have been previously synthesized,[24−38] most require two-step syntheses consisting of either polysiloxane macromers grafted onto fluorocarbon backbones or perfluorinated side chains grafted onto polysiloxane backbones[25−27,33] and consequently result in low molar mass products (M_w = 20−60K).[33] Alternatively, Boutevin et al.[30] and Babb et al.[34] have reported the synthesis of low molar mass linear fluorosilicone polymers by multistep condensation reactions. Few have synthesized fluorocarbon−siloxane polymers by radical polymerization in supercritical fluid $scCO_2$. DeSimone et al. synthesized fluorooctyl methacrylate/poly(dimethylsiloxane)-terminated methacrylate (FOMA−PDMSMA) and fluorooctyl methacrylate/tris(trimethylsilyl)propyl methacrylate (FOMA−SiMA) fluoro-copolymers in $scCO_2$;[35,36] however, both fluorocarbon and siloxane moieties were pendant to the hydrocarbon main chain, limiting overall thermal stability and chemical resistance.

Our goal was to synthesize a thermally stable, elastomeric and hydrophobic polymer. We chose to focus on synthesizing fluorosilicone polymers in $scCO_2$ by free

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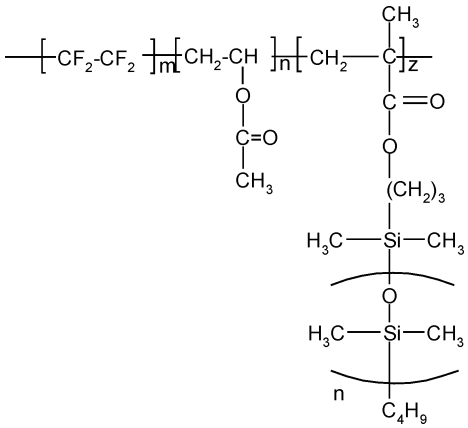
10.1021/ma047792s CCC: $30.25 © 2005 American Chemical Society
Published on Web 06/01/2005

Scheme 1. Chemical Structure of P(TFE-ter-VAc-ter-PDMSMA)



radical polymerization, having a fluorocarbon backbone and a siloxane pendant group. The fluorocarbon backbone is advantageous for thermal and chemical stability (and hydrophobicity) while the siloxane pendant group is advantageous for low surface tension and elasticity where the free volume of rotation associated with the siloxane pendant groups provides flexibility to the polymers. Using a one-step radical polymerization reaction in $scCO_2$, three monomers were copolymerized: methacryloxypropyl poly(dimethylsiloxane) methacrylate-terminated (PDMSMA), tetrafluoroethylene (TFE), and vinyl acetate (VAc), the latter of which was required for copolymerization of PDMSMA and TFE and allowed us to build on the linear fluoropolymer structures possible by synthesis in $scCO_2$ (see Scheme 1).[10]

Experimental Section

Reagents. All chemicals were purchased from Aldrich Chemical Co. (Ontario, Canada) and used as received unless otherwise specified. Methacrylate-terminated methacryloxypropyl poly(dimethylsiloxane) (M_w = 800−1000 g mol^{-1}, $n \approx 8$) was purchased from Gelest Inc. (Pittsburgh, PA) and used as received. TFE was prepared by vacuum pyrolysis of PTFE[39] and stored at room temperature over D-limonene in a 300 mL stainless steel sample cylinder fitted with an 1800 psi safety rupture disk. [*Caution: Tetrafluoroethylene is inherently dangerous. Anyone contemplating handling TFE under high pressure should familiarize himself or herself with safe handling procedures. TFE can explode with the force of TNT.*] Water was deionized and distilled from Millipore Milli-RO 10 Plus and Milli-Q UF Plus (Bedford, MA) systems and used at 18 MΩ resistance. The curative package bisphenol AF/quaternary phosphonium chloride was purchased from Dupont Co. (DE).

Synthesis of Fluoro-Terpolymers: P(TFE-ter-VAc-ter-PDMSMA). Polymerizations were conducted in a CO_2 high-pressure reactor as previously described.[10,11] Briefly, the free radical initiator, Vazo 64 (0.6% w/w), was recrystallized from methanol, dried in a vacuum oven for several hours at room temperature, and then introduced into the reactor. The reactor was evacuated and cooled to −50 °C, after which VAc and PDMSMA were added by cannula and then degassed prior to the addition of gaseous TFE, for a total monomer mass of 20 g. A 10% w/w of 1,1,2- trichloro-1,2,2-trifluoroethane (Freon113) was added to all polymerization mediums and used as a cosolvent to CO_2 to enhance the solubility of TFE macroradicals formed in CO_2. SCF purity CO_2 (Matheson, Ontario, Canada) was added and maintained at a pressure of 20−40 bar while warming the reactor to approximately 5 °C, at which temperature CO_2 was condensed into the reactor at a pressure of 55 ± 5 bar. The reactor was then heated to 65 ± 1 °C, and the pressures were initially between 330 and 350 bar. The polymerizations were stopped after 72 h by cooling the reactor and slowly venting to atmospheric pressure.[35] The white and tacky solid polymer that formed in the reactor was dissolved in dichloromethane or methyl ethyl ketone, quantitatively removed, and precipitated into a mixture of methanol/water to give the final purified polymer.

The feed compositions of TFE, VAc, and PDMSMA used are summarized with the results in Table 1. Yield was determined by mass of the final isolated terpolymer relative to the mass of the feed monomers.

Film Preparation and Cross-Linking. P(TFE-ter-VAc-ter-PDMSMA) terpolymer films were cross-linked according to the procedure described by Jacks et al. for Viton.[40] Briefly, films were prepared by dissolving 15% w/v polymer in methyl ethyl ketone (MEK) and then pouring this solution onto Teflon-coated glass sheets within a cylindrical mold, where the solvent was allowed to evaporate at room temperature and pressure overnight. Cross-linked fluorosilicone films were prepared by dispersing 2.7% MgO and 4% $Ca(OH)_2$ in MEK, to which the 15% w/v fluorosilicone polymer solution containing 2% (w/v) of bisphenol AF/quaternary phosphonium chloride in MEK was added, and homogenizing for at least 15 h prior to casting on a Teflon-coated glass sheet. The solvent evaporated overnight, and the dried film was precured at 145 °C for 30−60 min and then postcured at 204 °C for 16 h.

Bulk Characterization. Polymer molar mass was measured by gel permeation chromatography (GPC, Waters U6K injector, 510 pump) equipped with a refractive index detector (Waters 2410) and a series of Ultra-styragel columns (Waters 10^6, 10^4, and 500 Å). Using THF as the mobile phase at a flow rate of 1 mL min^{-1}, polymer molar mass was calculated relative to polystyrene standards. ^{1}H and ^{19}F NMR spectra (Varian Gemini spectrometer) were obtained in $CDCl_3$ at 399.95 and 376.30 MHz, respectively, with α,α,α-trifluorotoluene used as an internal reference. The fraction of TFE ($\bar{F}_{TFE}$) in the P(TFE-ter-VAc-ter-PDMSMA) terpolymer was calculated using ^{1}H and ^{19}F NMR data (see Figure 1) by referencing the VAc methine, PDMSMA methyl and TFE resonances to the proton and fluorine resonance of α,α,α-trifluorotoluene, respectively, as outlined in eq 1:

$$\bar{F}_{TFE} = \frac{3A_{TFE}/4A_{trifluoromethyl}}{3A_{TFE}/4A_{trifluoromethyl} + 5A_{methine}/A_{aryl} + 5A_{(methyl/54)}/A_{aryl}} \quad (1)$$

A_{TFE} and $A_{trifluoromethyl}$ are the integral areas of ^{19}F NMR tetrafluoroethylene and α,α,α-trifluorotoluene trifluoromethyl resonances, respectively. $A_{methine}$, A_{aryl} and A_{methyl} are the integral areas of the VAc methine and α,α,α-trifluorotoluene aromatic and PDMSMA methyl ^{1}H NMR resonances, respectively.

The fractions of VAc ($\bar{F}_{VAc}$) and PDMSMA ($\bar{F}_{PDMSMA}$) in the P(TFE-ter-VAc-ter-PDMSMA) fluoropolymer were calculated using ^{1}H NMR as outlined in eqs 2−3:

$$\bar{F}_{PDMSMA} + \bar{F}_{VAc} = 1 - \bar{F}_{TFE} \quad (2)$$

$$\bar{F}_{VAc} = \frac{A_{methine}}{A_{methine} + A_{methyl}}(1 - \bar{F}_{TFE}) \quad (3)$$

$A_{methine}$ and A_{methyl} are the integral area of VAc methine and PDMSMA methyl groups [$-Si(CH_3)_2-O-$], respectively.

Glass transition temperature (T_g) was measured using a differential scanning calorimeter (DSC, TA 2010, and TA Q1000), under an inert nitrogen atmosphere, with a heating rate 10 °C/min and scanning range of −160 to 100 °C. Thermogravimetric analysis (TGA) was performed using a TA, Q50 instrument under compressed air atmosphere, with a heating rate of 5 °C/min and scanning range of 35−600 °C. (A stable baseline was obtained for both DSC and TGA instruments.) Mechanical properties of cross-linked fluorosilicone films were tested using a micromechanical tester (Mach-1, Biosyntech, Montreal, QC), where the film sample, having dimensions of 210 ± 10 μm thick, 10 mm width, and 15−

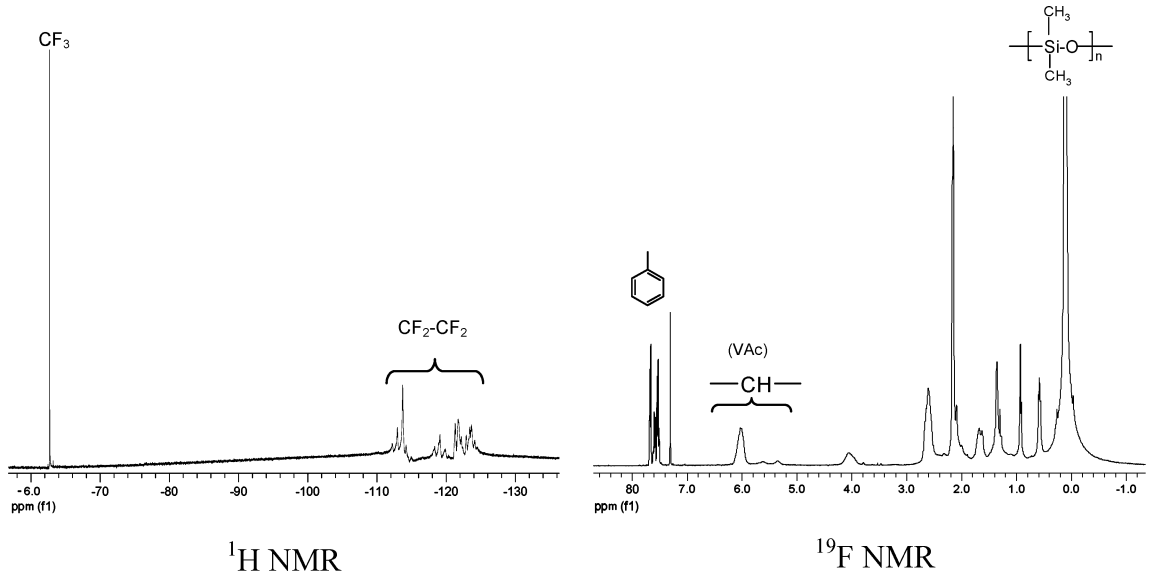


Figure 1. Representative ^{1}H and ^{19}F NMR spectra of P(TFE-ter-VAc-ter-PDMSMA) terpolymer with the composition 55.2−33−11.8 mol %.

Table 1. Bulk Characterization of P(TFE-ter-VAc-ter-PDMSMA) Fluoro-Terpolymers

composition (mol % in feed) P(TFE/VAc/PDMSMA)	yield (%)	composition (mol % in terpolymer) P(TFE/VAc/PDMSMA)[a]	P(PDMSMA) domains T_g (°C)	P(TFE−VAc) domains T_g (°C)	T_m (°C)	M_w/M_n/PDI (kg mol^{-1})
64.4/33/2.6	64	40.4/57.4/2.2	−119	38		173/53/3.3
77.2/20.2/2.6	56	46.3/47/6.7	−118	31		130/36/3.7
88/9.5/2.6	41	55.2/33/11.8	−120	28	235	87/35/2.4
94.3/3.4/2.3	32	67.6/13/19.3	−121		271	29/20.5/1.4
93.8/0/6.2	25	0/0/100	−122			27/15/1.8

[a] Composition determined by a combination of ^{1}H and ^{19}F NMR data.

25 mm length, was pulled in tension at a speed of 1 mm/min (n = 2−3 terpolymer films for each composition).

Surface Characterization. All fluorosilicone films were washed with pentane to dissolve any adsorbed silicone contaminants that may exist on the film surface and then dried at room temperature for several hours. Advancing and receding water contact angles were measured on film surfaces (exposed to air) using a Ramé-Hart NRL telescopic goniometer equipped with a Gilmont syringe and a 22-gauge flat-tipped needle. The data presented are the average and standard deviation of at least six measurements made at different areas on the film surface; three different films of each terpolymer composition were tested for that purpose. All contact angles had standard deviations of 1°−4°.

Surface elemental composition was determined by X-ray photoelectron spectroscopy (XPS, Leybold LHMax 200) using an Al Kα X-ray source at 15 kV and 25 mA emission current. Data were collected at takeoff angles of 90° and 20° (between the sample plane and detector), and samples were exposed to the X-ray for less than 5 min using pass energies of 192 and 42 eV for survey and C_{1s} region spectra, respectively. X-ray damage of film surfaces was negligible under these conditions.

Results and Discussion

As shown in Table 1, a series of fluoro-terpolymers P(TFE-ter-VAc-ter-PDMSMA) were synthesized in supercritical fluid CO_2 and characterized for yield, bulk composition, molar mass, T_g, and T_m.

As shown, when TFE and PDMSMA were copolymerized together in the absence of VAc, only PDMSMA homopolymers resulted, with no evidence of TFE in the copolymer as determined by ^{1}H and ^{19}F NMR. This lack of copolymerization between TFE and PDMSMA likely results from the significant disparity of monomer reactivity. Interestingly, Weise et al. [41] also found that TFE and MMA would not copolymerize without the incorporation of a third monomer, methyl trifluoroacrylate (MPFA), which cross-propagates with both TFE and MMA macroradicals to produce a P(TFE-ter-MPFA-ter-MMA) terpolymer. We found that the VAc monomer was necessary to copolymerize TFE with PDMSMA, resulting in P(TFE-ter-VAc-ter-PDMSMA) terpolymers.

Table 2. CO_2 Copolymerization of VAc (f_{VAc}) with PDMSMA to Low Conversion To Determine VAc Composition in the Copolymer (F) and Thus Reactivity Ratios

f_{VAc} (mol %)	yield (wt %)	F_{VAc} (mol %)	M_w/M_n (kg mol^{-1})	PDI
97.3	8.5	66.7	98/56	1.75
95.5	7	46	92/54	1.7
91.3	8.5	33	114/69	1.65
88.4	11	26.2	113/67	1.67
93.3	10	41.2	92/53	1.72
93.3	10	40.3	92/53	1.72
93.3	10	40.4	92/53	1.72

To gain a greater understanding of the lack of TFE-PDMSMA copolymer formed, we investigated the reactivity ratios of TFE−VAc copolymers and VAc−PDMSMA copolymers. Using the error-in-variables model (EVM),[42] we previously reported reactivity ratios for TFE−VAc copolymers synthesized in $scCO_2$ of $r_{TFE} \approx 0$ and $r_{VAc} = 0.95 \pm 0.08$, indicating that the radical on TFE cross-propagates with VAc whereas the radical on VAc propagates randomly.[11] Using the same methodology, the reactivity ratios for VAc−PDMSMA copolymers were calculated in $scCO_2$. The polymerization results for P(VAc-*co*-PDMSMA) are summarized in Table 2.

To estimate reactivity ratios by EVM, error estimates were required for both the monomer feed and copolymer composition. An error estimate of 5.7% was used for

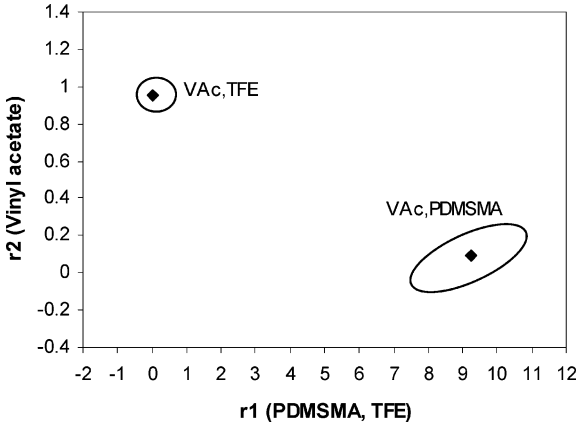


Figure 2. Estimated reactivity ratios and 95% confidence ellipses for the CO_2-polymerized copolymers: (◆) P(TFE-*co*-VAc) and (■) P(VAc-*co*-PDMSMA).

monomer feed compositions, reflecting the precision of gravimetric measurements and estimated monomer purity. Error estimates of 0.5% was used for P(VAc-*co*-PDMSMA) copolymer compositions, reflecting the copolymer purity and the standard deviation for three separate NMR elemental analysis measurements at the same composition (cf. the last 3 entries in Table 2). Figure 2 is a graphical representation of the estimated reactivity ratios for all copolymer series and their respective 95% confidence ellipses.

Under CO_2 copolymerization condititions, $r_{VAc} = 0.09 \pm 0.04$ and $r_{PDMSMA} = 9.26 \pm 1.9$, indicating that the radical on VAc cross-propagates with PDMSMA and the radical on PDMSMA mainly self-propagates. The reactivity ratio of PDMSMA is likely underestimated relative to VAc given the bulky polysiloxane side chain that sterically hinders the PDMSMA radicals.[35] Thus, it is perhaps not surprising that TFE−PDMSMA copolymers did not form, given the disparity in reactivity ratios between PDMSMA and VAc, VAc and TFE, and, by implication, TFE and PDMSMA, where TFE is estimated to have a reactivity ratio 4 orders of magnitude less than that of PDMSMA.

To enhance copolymerization of TFE and PDMSMA, VAc was included in the monomer feed; terpolymers resulted of TFE−VAc−PDMSMA as determined by ^{1}H and ^{19}F NMR. As shown in Table 1, monomer feed composition influenced terpolymer composition. We fixed the mole fraction of PDMSMA in the feed at 2.3−2.6 mol % and investigated the molar ratio between TFE and VAc. We wanted to minimize VAc content in the terpolymer because it is the least thermally stable of the three monomers and maximize the TFE content because it is the most thermally stable. For all polymers synthesized, the mole fractions of TFE in the terpolymers were lower than those in the feed whereas the opposite behavior was observed for VAc monomers. This may be due to the fact that VAc is more reactive than TFE. When the mole fraction of VAc in the feed was only 3.4 mol %, the terpolymer composition and properties were affected dramatically. Since TFE likely cross-propagates only in the presence of VAc, with decreased VAc, there is a higher propensity for TFE to self-propagate and potentially form crystalline segments. Moreover, with lower concentrations of VAc in the feed, the mole fraction of PDMSMA in the terpolymer increased significantly likely because PDMSMA more readily self-propagates than cross-propagates. On the basis of previous data where no transfer to VAc from TFE was observed,[10] we assumed the same to be true here.

The molar masses of the fluoro-terpolymers were high yet decreased significantly with decreased VAc concentration. For example, the terpolymer molar mass decreased significantly from 173 to 29 kg mol^{-1} as the mole fraction of VAc decreased from 57.4 to 13.1 mol % in the terpolymer. Terpolymer yield also decreased with VAc mol %, from 64% for 57.4 mol % to 32% for 13.1 mol % in the terpolymer. Given that VAc is required for TFE and PDMSMA to be copolymerized, the correlation of VAc with both molar mass and yield is the critical correlation. Without VAc, low molar mass PDMSMA homopolymers resulted likely due to steric hindrance associated with the PDMS pendant group and the yield decreased further to 25%.

The solubility of these terpolymers decreased with increasing TFE content in the terpolymer, suggesting that short repeats of crystalline TFE may have formed along the polymer backbone. For example, terpolymers with 55.2 mol % TFE formed a translucent solution when dissolved in MEK or chloroform whereas terpolymers with 67.6 mol % TFE were insoluble and only swelled in MEK or chloroform.

The DSC thermograms reflected terpolymer composition. For example, terpolymers having ≤55.2 mol % of TFE showed two glass transitions, indicating a two-phase morphology. The first transition, between 28 and 38 °C, is attributed to P(TFE−VAc) domains whereas the second transition, between −118 and −121 °C, is attributed to P(PDMSMA) domains. The T_g of the P(PDMSMA) domain is likely unaffected by composition because, as suggested by the monomer reactivity ratios, PDMSMA self-propagates and P(PDMSMA) likely forms microphase-separated regions. Interestingly, these results are consistent with those of polymers of similar compositions.[35] However, the T_g of the P(TFE−VAc) domains is affected by the mole fraction of P(PDMSMA) in the terpolymer: while there is no impact on the P(TFE−VAc) T_g of 38 °C for low concentrations of PDMSMA of 2.2 mol % in the terpolymer, the T_g associated with P(TFE−VAc) decreased to 31 °C and then to 28 °C as PDMSMA mole fraction in the terpolymer increased to 6.7 mol % and 11.8 mol %, respectively. The siloxane groups may act as plasticizers for the P(TFE−VAc) domains, thereby lowering T_g. Interestingly, the DSC thermogram of the terpolymer having 67.6 mol % of TFE did not have a T_g, which may simply be a reflection of the low concentration of VAc present and thus the decreased propensity of having P(TFE−VAc) amorphous domains; however, a sharp peak representing a melting transition of the crystalline TFE segments was observed at 271 °C (see Figure 3). A melting transition was also observed for the 55.2 mol % TFE terpolymer, but not for the other polymers with lower TFE concentration.

The formation of TFE crystalline segments indicates that the TFE macroradical can self-propagate due to a favorable interaction with CO_2. Cross-linking these terpolymers did not substantially affect the T_g, which decreased with increasing PDMSMA mol % in the terpolymer, from 36 °C for 2.2 mol % to 34 °C for 6.7 mol % to 27.5 °C for 11.8 mol %.

Surface Characterization of Fluorosilicone Terpolymer Films. Both un-cross-linked and cross-linked fluorosilicone terpolymer films were cast from methyl ethyl ketone onto glass slides, and the air−polymer

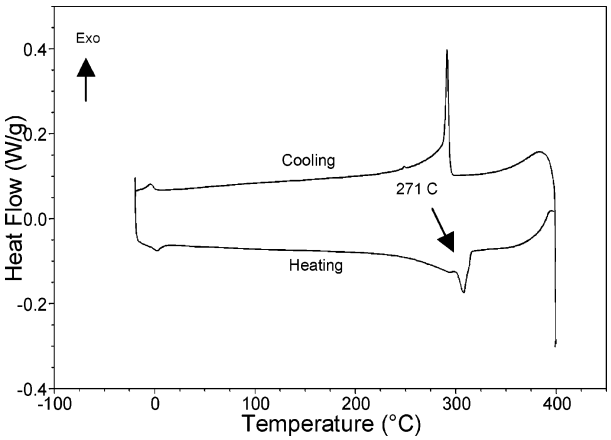


Figure 3. DSC thermogram of P(TFE-ter-VAc-ter-PDMSMA), 67.6/13/19.3 mol %. The T_m is 271 °C.

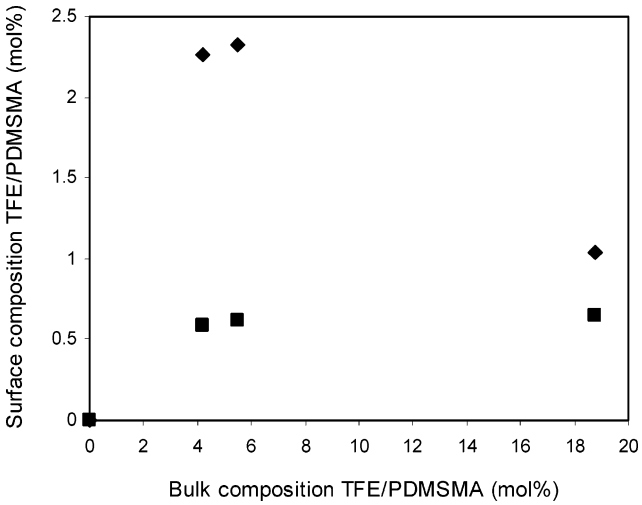


Figure 4. Comparison at the air−polymer surface of (◆) un-cross-linked and (■) cross-linked P(TFE-ter-VAc-ter-PDMSMA) terpolymers by XPS analysis at 90° takeoff angle. The ratio of TFE/PDMSMA at the surface is compared to that of the bulk, where fluorine atomic concentration represents the concentration of TFE and silicon atomic concentration represents the concentration of PDMSMA.

surface was analyzed by dynamic advancing and receding water contact angles and XPS. As shown in Table 3, the advancing water contact angles for both un-cross-linked and cross-linked fluoro-terpolymer films are high and increase with increasing TFE and PDMSMA concentrations in the terpolymer. Moreover, the advancing water contact angles are greater for the cross-linked vs un-cross-linked analogues. The receding contact angles also increased with TFE and PDMSMA concentration in the terpolymer; however, these values were significantly lower and reflected the hydrophilic species (i.e., VAc) present at the surface. The receding contact angles also increased with cross-linking.

To better understand the hydrophobic nature of the fluoro-terpolymer films, both un-cross-linked and cross-linked air−polymer surfaces were analyzed for elemental composition by XPS at takeoff angles of 90°, reflecting the top 100 Å, and 20°, reflecting the top 40 Å. XPS-determined surface compositions were compared to NMR-determined bulk compositions (from Table 1), as summarized in Figure 4 in terms of TFE/PDMSMA mol % ratios. As shown in Figure 4, the molar ratio TFE/PDMSMA at the air surface is smaller than that in the bulk for both un-cross-linked and cross-linked terpolymer films where the difference is more pronounced for the cross-linked films and at a 20° XPS takeoff angle (data not shown). These results indicate siloxane groups of PDMSMA are enriched at the surface relative to TFE. Siloxane groups likely enrich the surface due to a lower critical surface tension of 21 dyn/cm relative to that of TFE of 24 dyn/cm (and that of PVAc of 36.5 dyn/cm).[43] The siloxane groups have greater mobility than the TFE groups because they are pendant to the main chain and thus have greater free volume of rotation and can orient themselves at the air−polymer surface. Moreover, the very low T_g associated with the PDMSMA domains facilitates mobility. The cross-linking process itself, of heating at 204 °C for 16 h, enhances chain mobility and allows the polymer chains to reorient further to lower interfacial free energy and greater siloxane enrichment of the surface. Last, differences in polarity values (as tabulated in the *Polymer Handbook*)[43] among PVAc (0.329) and PTFE (0.089) and PDMS (0.042) may also account for surface enrichment of PDMS as polarity is correlated with surface tension.

Thermal Properties of Fluorosilicone Terpolymer Films. The thermogravimetric (TG) traces for all un-cross-linked fluoro-terpolymers are included in Figure 5. All terpolymer samples were heated from room temperature to 600 °C at a fixed heating rate of 5 °C/min in air, and plots of mass loss vs temperature are shown. To gain a greater understanding of the degradation behavior of the fluorosilicone terpolymers, PTFE, PVAc, and P(PDMSMA) homopolymers were compared with those of fluoro-terpolymers P(TFE-ter-VAc-ter-PDMSMA) at two specific degradation temperatures: (1) the temperature of the initial (1%) mass loss ($T_{1\%}$) and (2) the temperature at 50% mass loss ($T_{50\%}$). These data are summarized in Table 4. On one hand, all of the terpolymers have $T_{1\%}$ values between 238 and 244 °C, which are most similar to that of PVAc of 244 °C and seem to be mostly independent of composition. It is known that at 244 °C acetic acid is eliminated from PVAc[44] (see Scheme 2), and this likely accounts for the $T_{1\%}$ data of all of the terpolymers. On the other hand, the $T_{50\%}$ values seem to be dependent on fluoropolymer content, increasing from 369 to 410 °C as TFE concentration increased from 40.4 to 67.6 mol % in the terpoly-

Table 3. Dynamic Advancing and Receding Water Contact Angles of Un-Cross-Linked and Cross-Linked Fluoro-Terpolymer Films (n = 3 Different Films and Six Measurements per Film, Mean ± Standard Deviation)

terpolymer compositions P(TFE/VAc/PDMSMA) mol %	films	advancing contact angle (deg)	receding contact angle (deg)
40.4/57.4/2.2	un-cross-linked	97 ± 3	54 ± 2
	cross-linked	105 ± 2	58 ± 2
46.3/47/6.7	un-cross-linked	100 ± 2	60 ± 2
	cross-linked	111 ± 1	64 ± 2
55.2/33/11.8	un-cross-linked	112 ± 4	69 ± 2
	cross-linked	125 ± 3	81 ± 2

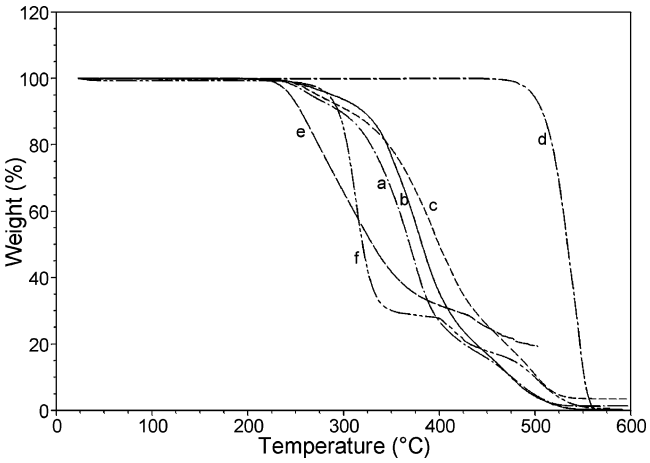
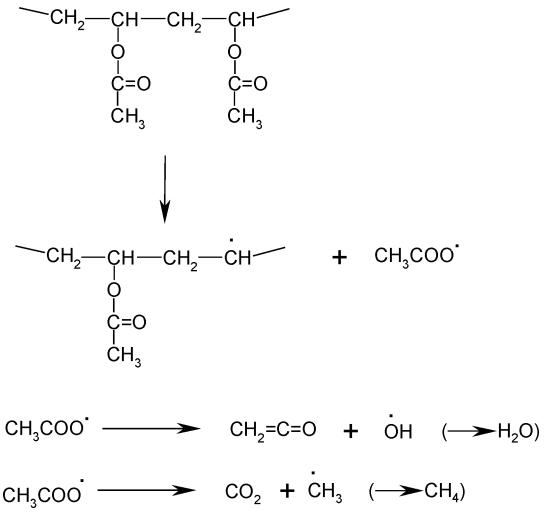


Figure 5. Comparison of TGA curves between un-cross-linked terpolymers, P(TFE-ter-VAc-ter-PDMSMA): (a) 40.4/57/2.2 mol %; (b) 46.3/47/6.7 mol %, (c) 55.2/33/11.8 mol %; (d) PTFE, (e) PPDMSMA, and (f) PVAc.

Table 4. Thermogravimetric Analysis of Un-Cross-Linked and Cross-Linked Fluoro-Terpolymers, PTFE, PVAc, and P(PDMSMA)

P(TFE/VAc/PDMSMA), mol %	un-cross-linked		cross-linked	
	$T_{(1\%\ w\ loss)}$	$T_{(50\%\ w\ loss)}$	$T_{(1\%\ w\ loss)}$	$T_{(50\%\ w\ loss)}$
40.4/57.4/2.2	238	369	260	378
46.3/47/6.7	244	382	270	387
55.2/33/11.8	243	400	292	412
67.6/13/19.3	240	410	265	422
PTFE	475	534		
PVAc	244	319		
P(PDMSMA)	226	330		

Scheme 2. Free Radical Mechanism for the Degradation of PVAc[43]



mer samples. Given that PVAc and P(PDMSMA) have significantly lower $T_{50\%}$ values than the terpolymers, TFE likely has the dominant effect of decomposition.

To gain a better understanding of the possible thermal degradation mechanism in the terpolymers, we investigated the thermal degradation mechanisms for PVAc and PDMSMA homopolymers. For PVAc thermal degradation, after acetic acid is eliminated at 244 °C, polyene sequences[44] are formed which then rearrange and decompose to aromatic and aliphatic hydrocarbons which degrade at 460 °C (Scheme 2). The acetate radicals formed from the deesterification of PVAc at

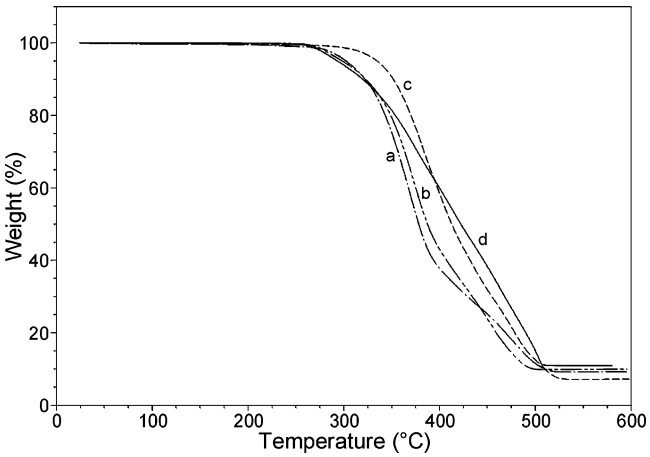
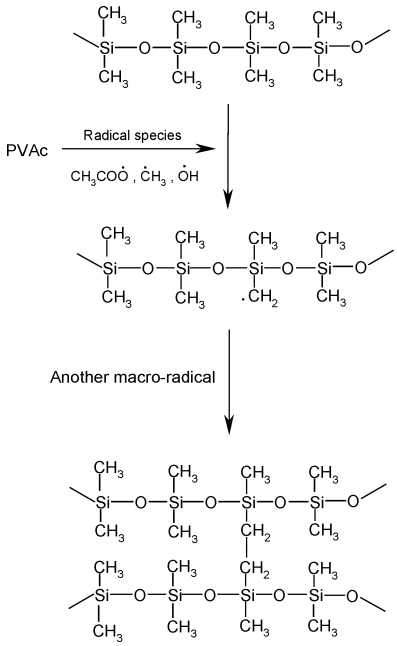


Figure 6. Comparison of TGA curves between cross-linked terpolymer compositions, P(TFE-ter-VAc-ter-PDMSMA): (a) 40.4/57/2.2 mol %; (b) 46.3/47/6.7 mol %, (c) 55.2/33/11.8 mol %; (d) 67.6/13/19.3 mol %.

Scheme 3. Cross-Linking of PDMS Results in Acetate Radicals[44]



244 °C may abstract hydrogen from pendant PDMS methyl groups of PDMSMA, and pairs of these macroradicals may cross-link (Scheme 3).[45] (Alternatively, free radicals generated in air may abstract these hydrogens.) The cross-linking of these PDMS macroradicals serves to stabilize PDMSMA because PMMA normally degrades around 230 °C due to unsaturated end groups and at 340 °C due to random segment scission.[46−48] Thus, the PDMS pendant groups of PDMSMA can be considered as MMA-pyrolysis inhibitors which trap free radicals generated from the thermal degradation of PVAc and, consequently, decelerate the thermal decomposition of PDMSMA.[44]

The thermogravimetric traces shown in Figure 6 and Table 4 for $T_{1\%}$ and $T_{50\%}$ summarize the thermal stability data of cross-linked terpolymer samples. As expected, on the basis of the greater activation energy required to destabilize a cross-linked (vs un-cross-linked) polymer network,[47,49] all cross-linked fluorosilicone terpolymer films are more thermally stable than un-cross-linked films (cf. Tables 4) at both $T_{1\%}$ and $T_{50\%}$

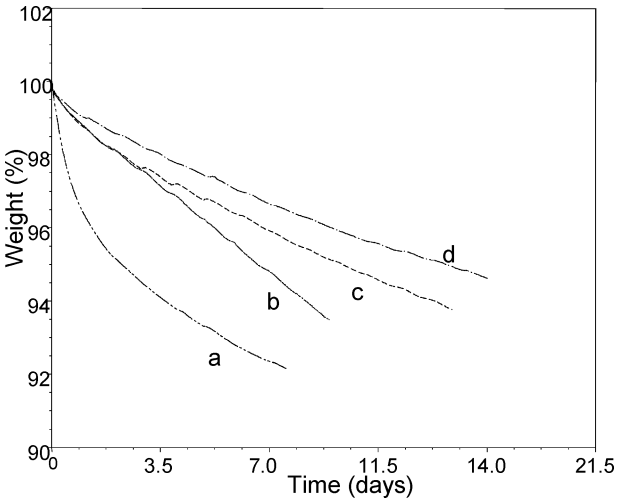


Figure 7. Prolonged thermal stability test at 200 °C of different terpolymer compositions was determined by mass loss over time for P(TFE-ter-VAc-ter-PDMSMA): (a) 67.6/13/19.3 mol %; (b) 40.4/57/2.2 mol %; (c) 46.3/47/6.7 mol %; (d) 55.2/33/11.8 mol %.

values, but the impact at $T_{1\%}$ is more substantive. This may reflect cross-linking of the acetate groups of PVAc, which become less susceptible to degradation due to cross-linking. Moreover, the thermal stability of cross-linked fluoro-terpolymers increased with TFE content in the terpolymer from 40.4 to 55.2 mol % for both $T_{1\%}$ of 260−292 °C and $T_{50\%}$ of 378−412 °C, respectively. Surprisingly, the fluoro-terpolymer having 67.6 mol % of TFE is less thermally stable than all other fluoro-terpolymer compositions, and this may be due to its lower molecular weight than other fluoro-terpolymer compositions. This suggests that there is an optimal composition and molecular weight for the fluoro-terpolymer that presents the best thermal stability, and it seems that both high TFE content along with high molecular weight will have a direct impact on the final thermal properties of the fluoro-terpolymer. For example, the optimal composition that we found for thermal stability is the cross-linked terpolymer having TFE content of 55.2 mol %, VAc of 33 mol %, and PDMSMA of 11.8 mol %.

To gain a greater understanding of the thermal behavior of these cross-linked fluoro-terpolymers, a prolonged thermal stability test at 200 °C was performed. As shown in Figure 7, the thermal stability increased with TFE content in the terpolymer from 40.4 to 55.2 mol %. The mass loss observed may be from that of the curative package of un-cross-linked repeat units or PVAc given that the curing mechanism likely involves abstracting VAc methylene protons and TFE fluorine atoms from two adjacent polymer chains (Scheme 4). To better understand the origin of mass loss due to prolonged exposure at 200 °C, we analyzed the air−polymer surface of two of these cross-linked terpolymer films by XPS at 90° and 20°. As shown in Table 5, the concentration of silicone and fluorine were essentially unchanged after 17 days of curing the polymer film at 200 °C in air, suggesting that the mass loss is not from the PDMSMA or TFE repeats. While only bulk elemental analysis would confirm that mass loss was not attributed to PDMSMA and TFE, it is unlikely that PDMSMA and TFE decomposed at these temperatures and simply had the surface PDMSMA and TFE compositions replenished at the air−polymer interface due

Scheme 4. Proposed Structure of P(TFE-ter-VAc-ter-PDMSMA), Cross-Linked by Bisphenol-AF (Ar in the Scheme) through the CH_2 Groups of VAc[40]

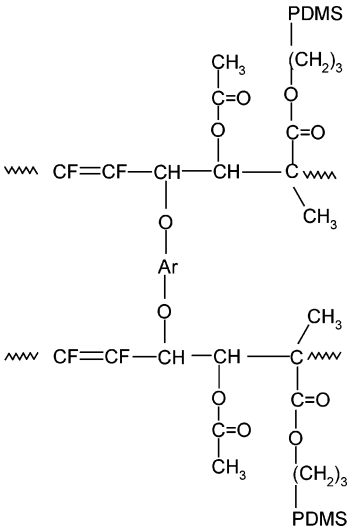


Table 5. Comparison of XPS Data of Cross-Linked P(TFE-ter-VAc-ter-PDMSMA) 55.2−33−11.8 mol % at Different Cross-Linking Times

curing time	XPS takeoff angle (deg)	C_{1s} (%)	O_{1s} (%)	F_{1s} (%)	Si_{2P} (%)
16 h	90	46.4	27.7	6.1	19.4
17 days	90	47.5	26.5	7.4	18.6
16 h	20	42.7	30.2	4.2	22.7
17 days	20	42.9	27.5	5	24.1

to surface organization. Overall, these fluorosilicone terpolymer films have excellent thermal stability. Surprisingly, the terpolymer with the highest TFE content of 67.6 mol % had the fastest thermal degradation, and this may be because this terpolymer had the lowest molecular weight compared to the other compositions. The optimal composition of the terpolymer that presents the best prolonged thermal stability has 55.2 mol % of TFE, 33 mol % of VAc, and 11.8 mol % of PDMSMA. These results are consistent with those for short-term thermal stability as well (Figure 7).

Mechanical Properties of Fluoro-Terpolymers Films. Cross-linked fluoro-terpolymer films were cast from methyl ethyl ketone and postcured for different times from 16 h to 30 days. All films were flexible and easy to handle except for the 67.6 mol % TFE terpolymer, which was brittle and difficult to handle, likely due to its low molar mass (cf. Table 1).

The stress−strain behavior was affected by both curing time and composition. As shown in Figure 8 for the fluoro-terpolymer film within 55.2 mol % TFE, both the yield strength and the elastic modulus increased with curing time. For example, the film cured for 16 h had a yield strength of 1.33 MPa and an elastic modulus of 23 MPa. Surprisingly, the yield strength and the elastic modulus increased with postcuring time of the fluorosilicone terpolymer films from 16 h to 30 days, indicating that the film became increasingly tough and stiff, reaching a yield of 7.6 MPa and elastic modulus of 80 MPa after 30 days. The continued increase in mechanical properties observed may be due to ongoing cross-linking of VAc and TFE repeats. In addition, the acetate radicals formed from the slow degradation of VAc units may attack the PDMSMA methyl groups by

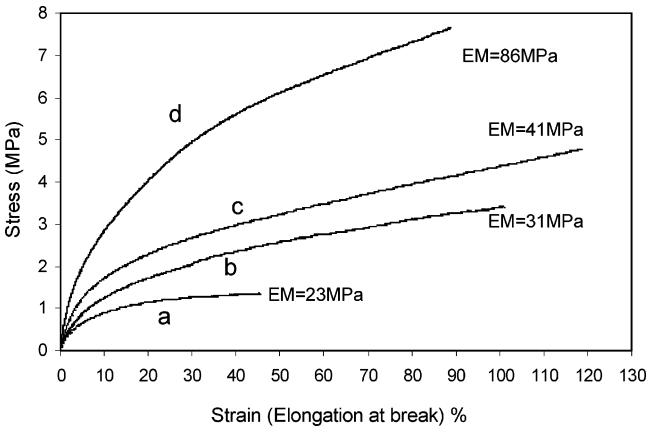


Figure 8. Representative stress−strain curves for P(TFE-ter-VAc-ter-PDMSMA), (55.2−33−11.8) mol %, with various postcuring times: (a) 16 h, (b) 10 days, (c) 17 days, and (d) 30 days. The elastic modulus (EM) for each is shown (n = 2−3 films).

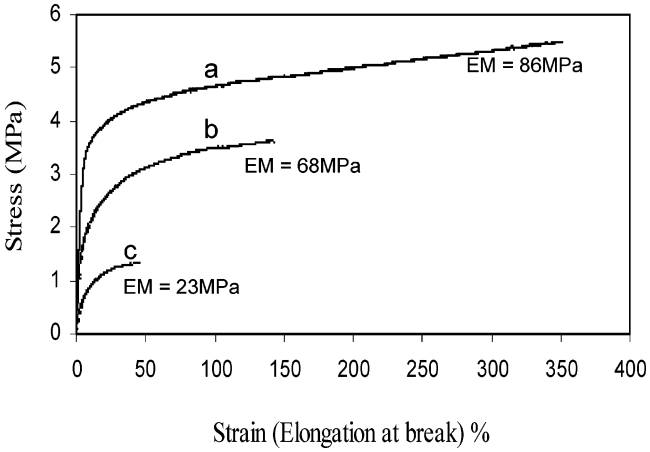


Figure 9. Comparison of representative stress−strain curves of different P(TFE-ter-VAc-ter-PDMSMA) compositions: (a) 40.4/57/2.2 mol %; (b) 46.3/47/6.7 mol %; (c) 55.2/33/11.8 mol %. The elastic modulus (EM) for each is shown.

abstracting protons from two adjacent polymer chains followed by cross-linking of the PDMS pendant groups, thereby making the fluoro-terpolymer film tougher than it was after cross-linking for only 16 h (Scheme 3). This suggests that the mass loss that occurred after the prolonged thermal stability test at 200 °C (Figure 8) was not a result of fluorosilicone terpolymer degradation, which seems stable for at least 30 consecutive days at 200 °C.

The mechanical properties were also affected by fluorosilicone terpolymer composition, where, as shown in Figure 9, both yield and elastic modulus increased with VAc concentration (and decreased with increased TFE content). This is consistent with the proposed cross-linking process of VAc methylene radicals reacting with PDMSMA methyl groups, resulting in the incorporation of high concentrations of bisphenol AF and tough fluorosilicone terpolymers. Moreover, the steep increase in elastic modulus, from 23 MPa for P(TFE-ter-VAc-ter-PDMSMA) of 55.2/33/11.8 to 86 MPa for that of 40.4/57.4/2.2, reflects the increase in amorphous domains associated with VAc and PDMSMA, which provide elasticity to the final cross-linked fluorosilicone terpolymer.

Conclusions

Hydrophobic, thermoplastic and thermally stable fluoro-terpolymers of P(TFE-ter-VAc-ter-PDMSMA) were successfully synthesized by free radical polymerization in supercritical fluid CO_2. The great difference in reactivity between TFE and PDMSMA necessitated the use of VAc for copolymerization of TFE with PDMSMA. P(TFE-ter-VAc-ter-PDMSMA) were stable for prolonged times at 200 °C, with thermal stability increasing with both TFE concentration and cross-linking. Fluorosilicone terpolymer films were hydrophobic due to a surface enrichment of PDMS pendant groups as confirmed by XPS. Moreover, these films were tough, with elastic moduli increasing with prolonged heating and VAc concentration. Overall, these fluoro-terpolymers provide significant advantages for coatings applications where tough, thermally stable, hydrophobic properties are required. In ongoing studies, we are investigating the use of these polymers as release agents for coatings applications.

Acknowledgment. We thank Dr. Peter Brodersen for his assistance in the XPS analysis and Prof. Ian Manners for use of his DSC. We are grateful to Peter Odell for an ongoing collaboration and to Xerox Research Centre of Canada and the Natural Sciences and Engineering Research Council of Canada for financial support through an NSERC CRD.

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MA047792S