New Poly(silanes-siloxanes) via Hydrosilation in Supercritical CO_2 and Subsequent Crosslinking

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Summary: In order to obtain crosslinkable, low dielectric, low Tg materials, the hydrosilation polymerization was carried out in supercritical carbon dioxide (SC CO_2) using Karstedt's catalyst, and a series of new fluorine-containing poly(carbosilane/siloxane) were synthesized and characterized. The molecular weights of polymers obtained in SC CO_2 were notably greater than those obtained in benzene. Hydrolysis and thermal curing of these polymers leads to materials considerably higher molecular weight which retain their low Tg values.

Introduction

Supercritical carbon dioxide has recently been the subject of extensive investigation for application as an extraction solvent and as a reaction medium. The driving force in these research efforts is the replacement of conventional organic solvents, many of which are toxic, with an inexpensive environmentally benign solvent. Although SC CO_2 has some inherent disadvantage as a potential reaction medium (poor solvent for polar molecules and most high polymers), the potential advantages to using it as a solvent and reaction medium are enormous. These advantages include its low cost, ready availability, easily accessible critical point, tunable density and solvent properties (through temperature and pressure variation), and ease of separation from reaction products. In addition it is a non-flammable, non-toxic naturally occurring component of the atmosphere, which is readily recycled. The use of SC CO_2 as a polymerization solvent, especially for free-radical polymerization, has received extensive study, has been extensively reviewed and remains an area of active investigation.[1]

One potentially important polymerization reaction, hydrosilation, has not been extensively studied in SC CO_2, even though this reaction has received considerable recent attention as a tool for synthesizing novel polymeric architectures. Examples include linear[2-4], comb[5], dendritic[6], hyperbranced[7-8] and crosslinkable[9-10] polymers. The first high molecular weight polymer has been synthesized by using Karstedt's catalyst, platinum-divinyltetramethyl-disiloxane (Pt-DVTMD), in conventional organic solvents[11].

As part of an ongoing research interest in crosslinkable, low dielectric, low Tg materials we

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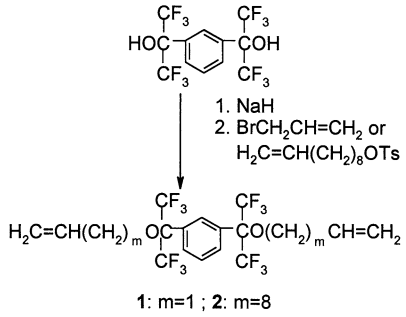
have utilized Karstedt's catalyst system to conduct hydrosilation polymerization reactions in SC CO_2[12]. In this paper we report more fully on that earlier communication and also report the synthesis and characterization of crosslinkable poly(carbosilane/siloxane)s by hydrosilation in toluene and SC CO_2.

Results and Discussion

Fluorine-Containing Poly(carbosilane/siloxane)s

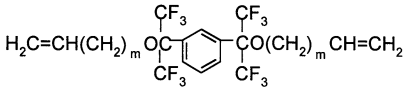
1,3-Bis(hexafluoro-2-hydroxy-2-propyl)benzene was selected as the source of fluorine in this series of polymers. It was first converted either to its diallyl ether derivative, **1,** or its bis(9-decenyl)ether derivative, **2** (**Scheme 1**). Model compound reactions with phenyldimethyl-silane were used to confirm that 1 and 2 undergo



Scheme 1

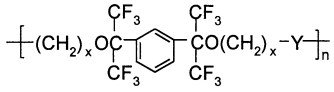
hydrosilation in SC CO_2 using either chloroplatinic acid or Karstedt's catalyst, (Pt-DVTMD), which was selected as the catalyst system for subsequent polymerization studies because of its good solubility in SC CO_2.

Monomers **1** and **2** have been reacted with selected disilane monomers, H-Y-H, to give two series of fluorine-containing polymers (**Scheme 2**). In all examples in both series of polymers, the samples prepared in SC CO_2 have greater molecular weights and, therefore, greater degrees of polymerization then analogues prepared in benzene (Table 1). This result indicates that SC CO_2 is a viable substitute solvent for this important reaction. It is also noted that polymers in the series in which x=3 (three methylene groups) are generally of lower molecular weight than analogues in which x=10 (ten methylene groups), and this molecular weight difference appears to be greater in SC CO_2 than in benzene. The origin of this



1: m=1 ; **2**: m=8

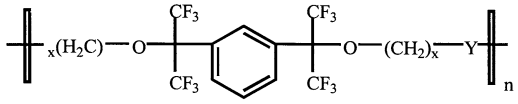
Disilane Co-monomer (H-Y-Y)
with [Pt-DVTMD]

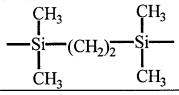
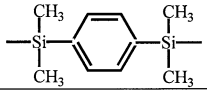
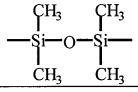
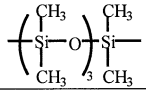
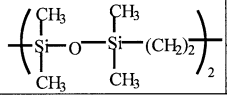


x=3 or 10

Scheme 2

Table 1. Polymers Molecular Weights – Benzene vs SC CO_2



Y	x	Mn*		Mw*		Polydispersity	
		Benzene	SC CO_2	Benzene	SC CO_2	Benzene	SC CO_2
	3	5200	8000	6600	10900	1.29	1.35
	10	7600	10700	13000	13300	1.70	1.25
	3	3500	5300	5100	8600	1.45	1.60
	10	6400	24600	10000	41700	1.53	1.69
	3	2700	3600	3500	4800	1.34	1.28
	10	5900	10000	12400	18700	2.10	2.05
	3	4900	10000	6300	15000	1.28	1.50
	10	4800	5100	9700	16700	2.01	1.60
	3	2400	4000	3000	5600	1.24	1.38
	10	9400	10600	13300	24900	1.40	2.34

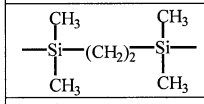
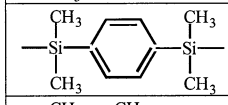
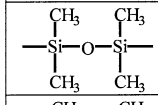
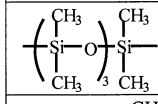
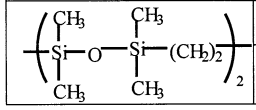
* by GPC

observation is not clear at this time but could be related to the difference in the steric requirements of monomers **1** and **2**. Monomer **1**, in which the double bond is separated from the bulky hexafluoroisopropoxy groups by a single methylene group, would be expected to have greater steric requirements which could affect its ability to coordinate to the platinum

catalyst. Polydispersities are somewhat scattered for both series of polymers but trend higher in the polymers wherein x=10 than in the x=3 analogues. The thermal stability of both series is only moderate as measured by TGA (Table 2). All of the polymers in both series have Tg values below 0°C and exist as colorless viscous liquids (Table 2). The lowest Tg values are found in the x=10 series of polymers containing disiloxane units in the backbone as expected[13].

Therefore, these polymers were selected for further synthetic elaboration into a crosslinkable polymer which retains the low Tg value.

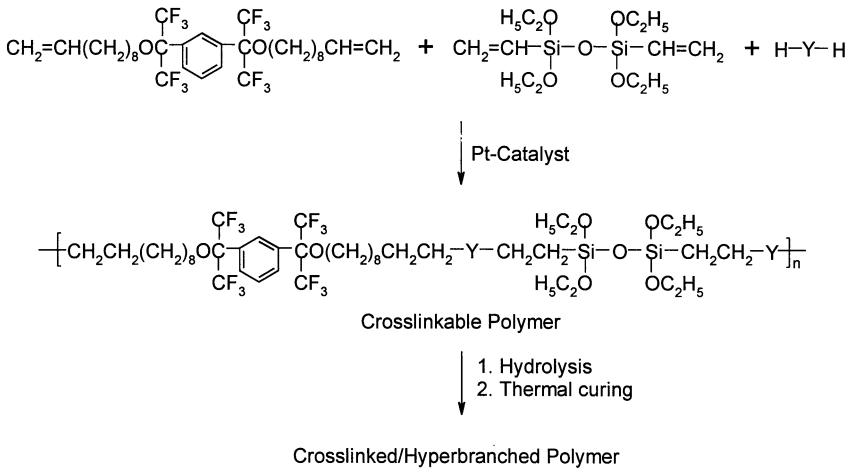
Table 2. Thermal Properties of Polymers

Y	x	Tg (°C)	TGA (10% wt loss)		% Char Yields (600°C)	
			Air	Argon	Air	Argon
	3	-26	287	291	2	0
	10	-38	330	397	2	1
	3	-41	321	307	4	0
	10	-32	289	306	2	0
	3	-53	249	265	1	1
	10	-67	314	376	4	1
	3	-48	317	350	4	0
	10	-59	307	354	6	0
	3	-50	268	283	4	1
	10	-59	336	368	3	5

Crosslinkable Ethoxysilane-Modified, Fluorine-Containing Poly(carbosilane /siloxane)s

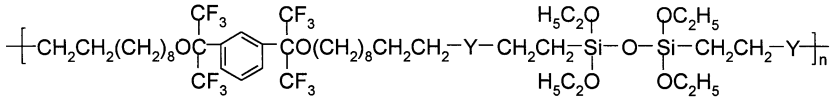
Crosslinkable ethoxysilane-modified_polymers were prepared as before from monomer **2** except that 1,1,3,3-tetraethoxy-1,3-divinyldisiloxane was added in place of 5% of the stoichiometric amount of the selected disilane, H-Y-H. This mixture was then reacted with disiloxane-containing disilanes in either toluene or SC CO_2 (**Scheme 3**).

The properties of these new polymers are summarized in Table 3. Somewhat higher molecular weight polymers were obtained in toluene solution although the reaction also proceeds in SC CO_2. No attempt was made to optimize reaction parameters in either solvent.



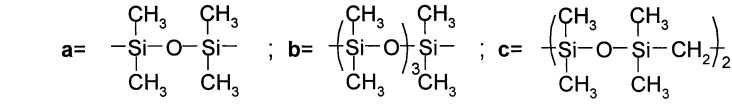
Scheme 3

Table 3. Polymer Properties Prior to Crosslinking (Chain Extension)



Y	$Mw^1 x10^{-3}$	PD	Tg^2 (°C)	TGA (°C 10% wt loss) Air	TGA (°C 10% wt loss) Argon	% Char Yield (@ 600°C) Air	% Char Yield (@ 600°C) Argon
a	10 SC CO_2	1.3	-54	278	304	7	3
	14 Toluene	1.8	-49	343	398	3	1
b	24 SC CO_2	2.4	-61	309	357	7	2.0
	41 Toluene	3.0	-63	360	416	4	1
c	38 Toluene	2.5	-56	346	405	4	1

[1.] Measured by GPC; [2.] Measured by DSC



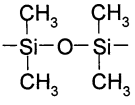
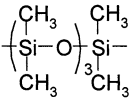
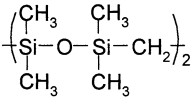
Polydispersities which ranged from 1.3 to 3.0 were more narrow in the two samples prepared in SC CO_2 than in analogous samples prepared in toluene. Thermal stability in this series of polymers is moderate and comparable to the noncrosslinkable analogues (Table 2). Importantly, glass transition temperatures remain low (-49° to -63°) in this series as expected for polymers with very flexible backbones.

The ethoxysilane-modified polymers are readily hydrolyzed by heating in wet diglyme (2% H_20) at 80°C for 24h. The uncured hydrolyzed polymers exhibited a broad IR band at 3200-3700 cm^{-1} which is characteristic of OH stretching in the silanol functionalities formed during hydrolysis. The polymers were then cured *in vacuo* at 135°C for 48h, after which time the intensity of the OH band was greatly diminished, but not totally absent. This thermal cure results in a considerable increase in molecular weight as condensation of silanol groups occurs.

Table 4. Polymer Properties[1] – After Crosslinking (Chain Extension)

Y	$Mw^2 x10^{-3}$	PD	Tg^3 (°C)	TGA (°C 10% wt loss) Air	TGA (°C 10% wt loss) Argon	% Char Yield (@ 600°C) Air	% Char Yield (@ 600°C) Argon
a	16 SC CO_2	2.3	-50	280	347	8	2
	56 Toluene	5.4	-46	320	397	5	0
b	113 SC CO_2	9.0	-60	309	380	8	2
	--[4] Toluene	--[4]	-59	346	417	4	1
c	156 Toluene	8.2	-55	296	403	8	1

[1.] Cured at 135 °C for 48 h in vaccum; [2.] measured by GPC; 3. measured by DSC
[4.] Dielectric constant = 2.63 @10 GHz

a=  ; **b=**  ; **c=** 

The properties of the thermally cured hydrolyzed polymers are summarized in Table 4. It is noted that the increases in molecular weight of these polymers is accompanied by a large increase in polydispersity as the silanol groups are condensed to disiloxane linkages. However, with the exception of one example, the polymers remain soluble suggesting that the establishment of the disiloxane bonds leads primarily to chain extension rather than

crosslinking. It is also important to note that the glass transition temperature of the polymers is essentially unchanged. Even in the case where the polymer became insoluble after hydrolysis and thermal cure, the value of Tg only changed by 4°C., from -63 to -59°C. The dielectric constant of this rubbery material was determined to be 2.63 at 10GHz.

Conclusions

It can be concluded that hydrosilation reactions in SC CO_2 proceed readily without complications. Using hydrosilation in SC CO_2 and in toluene, several new low Tg fluorinated poly(carbosilane/-siloxane)s with crosslinkable (or chain extendable) units have been synthesized. Hydrolysis and thermal curing of these polymers leads to materials of considerably higher molecular weight which retain their low Tg values. The dielectric constant of one of the cured polymers was determined to be 2.63 at 10GHz.

Acknowledgements

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