Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 3277–3285 **3277**
DOI: 10.1021/ma902798b

Novel Thermally Cross-Linkable Poly[(arylenedioxy)(diorganylsilylene)]s Based on Curcumin: Synthesis and Characterization

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Received December 18, 2009; Revised Manuscript Received March 6, 2010

ABSTRACT: Curcumin has attracted much attention due to its chemopreventive and anti-inflammatory properties. Here we describe the synthesis of poly[(arylenedioxy)(diorganylsilylene)]s via polycondensation between curcumin and various diorganodichlorosilanes. These novel polymers incorporate the β-diketone unit of curcumin as well as the Si−O bond in the backbone. The polymer structure was characterized by means of ^{1}HNMR, FTIR, and elemental analysis, while GPC results showed high molecular weights. Preliminary cell culture results suggest lack of cytotoxicity, which is important for potential applications such as implant and scaffold materials. The T_gs of these polymers are in the 24 to 131 °C range, tunable by altering the pendant organic groups. The un-cross-linked polymers are stable at 250 °C in air. The presence of vinyl groups in the backbone also allows the possibility for thermal cross-linking. DSC and rheology data demonstrate that the materials can cross-link at a temperature above 200 °C which suggests the feasibility of melt processing these polymers via a technique wherein a low viscosity polymer is made to flow into a heated mold where it cross-links over time and becomes a rigid thermoset material.

1. Introduction

Turmeric is a dried, ground rhizome of *Curcuma longa*, a perennial herb found commonly in Southeast Asia.[1] The use of this yellow powder as a spice and coloring agent in Indian cooking and as a therapeutic agent in traditional Indian and Chinese medicine has been known for centuries. Turmeric contains phenolic compounds called curcumoids that impart the characteristic yellow color.[2] Of these, curcumin [1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione], as the principle ingredient, accounts for about 77%; demethoxycurcumin for about 17% and bisdemethoxycurcumin about 3%.[3] All three curcumoids are diphenolic compounds.

In recent years, a large amount of experimental data has established the chemopreventive and chemotherapeutic properties of curcumin,[4−9] which has led to efforts toward drug development.[10,11] Jacob et al.[12] reported that the anti-inflammatory function of curcumin is perhaps one of its most important properties. Kohli et al.[13] and Chainani-Wu[14] published excellent reviews on the anti-inflammatory activity of curcumin. The anti-inflammatory properties of curcumin can be attributed to a large extent to its ability to inhibit the activation of NFK-β.[15−17] Curcumin has also been demonstrated to be effective against other diseases and biological conditions ranging from cystic fibrosis[18] and Alzheimer's disease[19] to malaria.[20] The promising biological effects of curcumin have led to a host of other review articles on the subject.[3,21−23]

In the field of polymer chemistry, curcumin has been used as an environment friendly and economical photoinitiator.[24,25] Suwantong et al.[26] and Gopinath et al.[27] reported the fabrication of curcumin containing electrospun cellulose acetate mats and curcumin incorporated collagen films, respectively, exploiting the anti-inflammatory function of curcumin. Raja et.al employed click chemistry to prepare a PAMAM dendrimer curcumin conjugate.[28] In addition, poly(vinyl chloride) was functionalized with curcumin by employing a nucleophilic substitution reaction to prepare a polymer that undergoes fluorescent quenching.[29] Curcumin was also used as a colorant for silicone based elastomers.[30] To the best of our knowledge, there has been only one report on the synthesis of a polymer using curcumin as a monomer. In this work, Matsumi et al.[31] synthesized polyesters by polycondensation of acid chlorides with the phenolic group of curcumin.

On the other hand, polysiloxanes (aka silicones) are often prepared by reacting dialkyl or diaryl dichlorosilanes with water, resulting in the elimination of hydrogen chloride.[32] The strength of Si−O bond imparts substantial thermal stability whereas its length provides greater flexibility and oxygen permeability to these materials.[33] Polysiloxanes are known to be highly biocompatible materials.[34,35] Srividhya et al.[36] have attributed the superior biocompatibility of polysiloxanes to their low chemical reactivity, hydrophobicity and low surface energy. These materials have found applications in contact lenses,[37] artificial heart valves,[38] medical adhesives,[39] etc. However, polysiloxanes, especially polydimethylsiloxane lack thermal rigidity and tend to exhibit "cold flow", especially at higher temperatures.[40,41] Further, thermally induced depolymerization is a limitation.[42] Addition of aromatic rings to the backbone provides rigidity to the structure and overcomes these drawbacks.[43] Copolymerization with curcumin accomplishes the addition of aromatic rings in the polymer backbone.

In this article, we present the synthesis of a series of poly[(arylenedioxy)(diorganylsilylene)]s through a polycondensation

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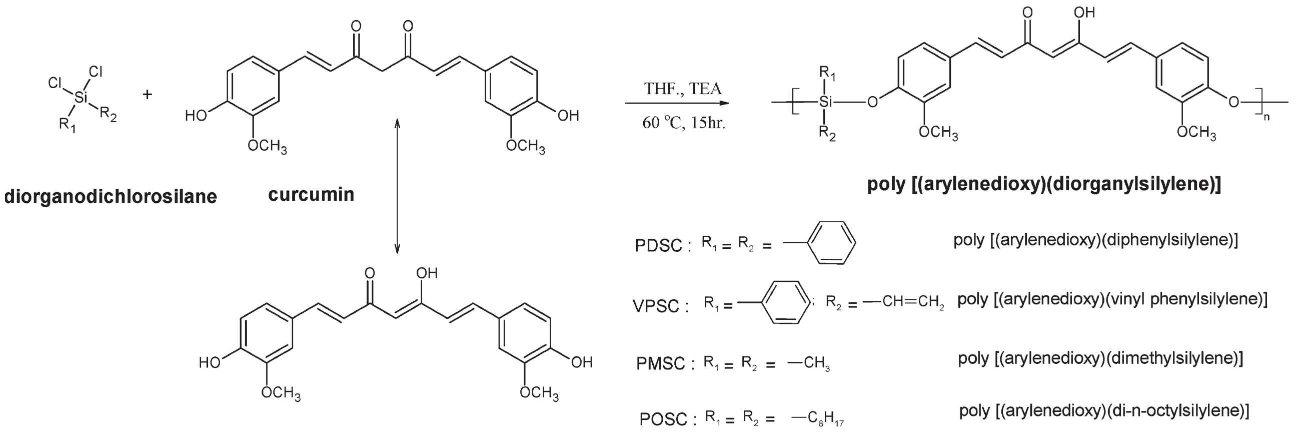
Scheme 1. Polycondensation of Diorganodichlorosilane with Curcumin for the Synthesis of Poly[(arylenedioxy)(diorganylsilylene)]s



reaction between diorganodichlorosilanes and the phenolic groups of curcumin (Scheme 1). The organic groups in diorganodichlorosilanes included phenyl, vinyl, methyl, and *n*-octyl groups that afforded poly[(arylenedioxy)(diphenylsilylene)] (PDSC), poly[(arylenedioxy)(vinylphenylsilylene)] (VPSC), poly[(arylenedioxy)(dimethylsilylene)] (PMSC), and poly[(arylenedioxy)(di-*n*-octylsilylene)] (POSC). They represent the first high molecular weight polymers that contain the β-diketone unit of curcumin as well as the Si−O bond in the backbone.

The curcumin repeat unit in the backbone of these polymers lacks the phenolic protons. While the excellent antioxidant properties of curcumin have been commonly ascribed to H abstraction from the phenolic units,[44,45] nonphenolic derivatives of curcumin (diarylheptanoids lacking phenolic OH) have also been shown to possess anti-inflammatory activity in at least three cases.[46−49] In fact, Jovanovic et.al state that “It is a common prejudice that a phenolic part of any molecule is *always* responsible for the antioxidant activity”, indicating that other parts of the molecule also contribute to this property.[50] They demonstrated that H atom abstraction from the methylene (CH_2) group of the β-diketone unit is also responsible for the antioxidant properties of curcumin. It is therefore possible that the materials described herein may find applications as implant or scaffold materials with reduced inflammation characteristics. Further, it is known in the literature that the acid or alkaline degradation of polysiloxanes (repeat unit: $-R_2Si-O-$) and polysilarylenesiloxanes (repeat unit: $-R_2Si-O-Ar-O-$) leads to the breakdown of the Si−O bond forming silanols (Si−OH).[51−53] Therefore, it can be expected that the curcumin unit in the backbone will be released upon slow degradation of these polymers within the body. The fact that one of the monomers, i.e., curcumin, is bioregenerable and derived from a perennial plant source is an added benefit.

This article reports the synthesis and characterization of these novel polymers. Studies on biocompatibility are underway and will be reported in a future work.

2. Experimental Section

2.1. Materials. Curcumin (mixture of curcumin, demethoxycurcumin, and bisdemethoxycurcumin), 98+% (cat. no. 218580100); triethylamine, 99% (TEA, cat. no. 15791), and tetrahydrofuran, anhydrous, 99.9% (THF, cat. no. 181500010) were purchased from Acros Organics. Diphenyldichlorosilane (cat. no. SID4510.1), dimethyldichlorosilane (cat. no. SID4120.1), di-*n*-octyldichlorosilane (cat. no. SID4400.0), and vinylphenyldichlorosilane (cat. no. SIV9092.0) were purchased from Gelest, Inc. Chloroform (Fisher BioReagents) and tetrahydrofuran were purified by distillation and were stored with molecular sieves. Methanol was obtained from Pharmco-Aaper. All other reagents were used as received.

2.2. Polymer Synthesis. The polycondensation between diorganodichlorosilane and curcumin was carried out in tetrahydrofuran (THF) solvent under nitrogen atmosphere in the presence of triethylamine (TEA) as HCl scavenger. Scheme 1 illustrates the general synthetic pathway followed.

In a typical procedure for the synthesis of poly[(arylenedioxy)(diphenylsilylene)]s (PDSC), 3.68 g (10 mmol) of curcumin, 2.13 g of TEA (21 mmol), and 15 mL of THF were charged into an oven-dried 50 mL three-neck round-bottom flask equipped with a magnetic stir bar, a Liebig condenser and a thermometer. The flask was immediately placed under nitrogen purge and heated to 60 °C. A flow of cold water through the condenser prevented the evaporation of THF and TEA. The reaction mixture became a red, nearly transparent solution at 60 °C. At this point, a solution of 2.66 g (10.5 mmol) of diphenyldichlorosilane in 15 mL of THF was added dropwise over a period of 60 min. The reaction mixture turned increasingly lighter in color until it acquired a yellow appearance. In the meantime, precipitation of triethylamine hydrochloride salt was observed. This yellow suspension was allowed to react for a further 15 h. Upon cooling to room temperature, 17 g of this suspension was added dropwise into 400 mL methanol. A yellow precipitate was obtained. This was the crude polymer. It was dried overnight in ambient conditions, following which it was resuspended in chloroform and filtered three times through fine pore (Whatman 42) filter paper (gravity filtration). The final filtrate was reprecipitated in methanol, after which it was dried overnight in a vacuum oven at 60 °C. This purified polymer was obtained as a yellow powder (80% yield).

2.3. Characterization. Molecular weights were determined using a Waters 590 (Waters Corp., Milford, MA) system equipped with a Phenogel 1μ 10^3 A column (Phenomenex, Torrance, CA) and a Waters 410 refractive index detector. Elution rate was maintained at 1 mL/min. THF was used as eluent for all cases and polystyrene standards were used for calibration. ^{1}HNMR and ^{13}CNMR spectra were obtained on a 500 MHz UnityInova instrument (Varian Inc., Palo Alto, CA). FTIR spectra were acquired on a Perkin-Elmer Spectrum One FTIR spectrometer (Perkin-Elmer Co., Norwalk, CT), using the attenuated total reflectance (ATR) mode. Differential scanning calorimetry (DSC) was performed using a heat−cool−heat cycle at a rate of 15 °C/min in nitrogen on a TA Q100 instrument (TA Instruments Inc., New Castle, DE). Thermogravimmetric analysis (TGA) was run in both nitrogen and air at 10 °C/min on a TA Q50 instrument. Images of the cell-proliferation on the polymer films were obtained using a phase contrast microscope (Nikon, Melville, NY). Elemental analysis was performed by Robertson Microlit Laboratories. Parallel plate rheology was performed on a AR2000 rheometer (TA Instruments Inc., New Castle, DE), equipped with 8 mm parallel plates and a 500 μm gap, under nitrogen. Shear rate was maintained at 10^{-5} s^{-1} with

Table 1. Structural and Molecular Weight Analysis of Poly[(arylenedioxy)(diorganylsilylene)]s: Summary of Results from GPC and Elemental Analysis

sample	diorganodichlorosilane	M_n	PDI	repeat unit MW	no. of repeat units	yield (%)	elemental analysis % C, % H (theor)	elemental analysis % C, % H (exp)
PDSC	diphenyldichlorosilane	15 100	2.11	548.66	28	80	72.24, 5.14	71.96, 4.86
VPSC	vinylphenyldichlorosilane	13 900	2.54	499.61	28	80	69.87, 5.26	69.74, 5.16
PMSC	dimethyldichlorosilane	9900	3.03	424.52	23	30	65.07, 5.70	64.89, 5.68
POSC	di-*n*-octyldichlorosilane	19 300	2.06	620.90	31	69	71.57, 8.44	71.45, 8.29

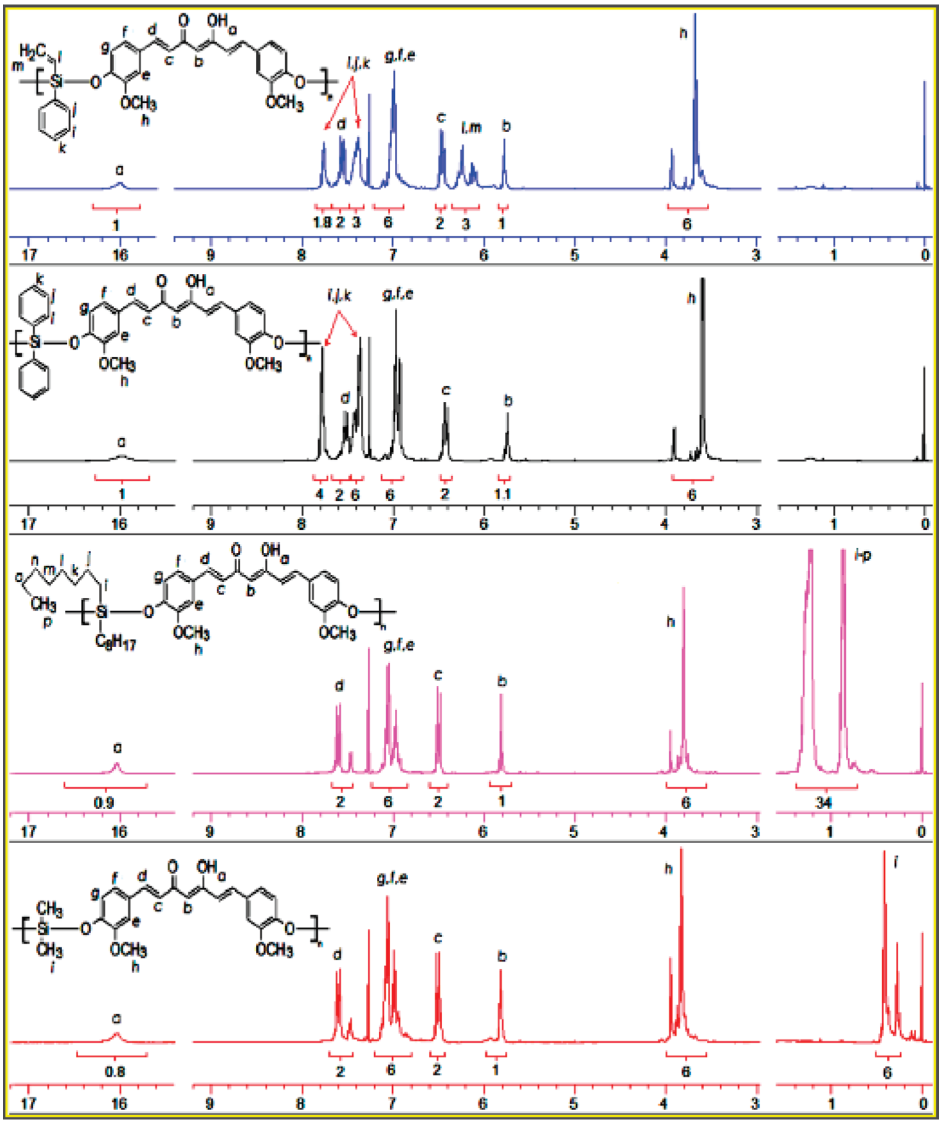


Figure 1. ^{1}HNMR spectra of poly[(arylenedioxy)(diorganylsilylene)]s with integration.

displacement at 1% strain (10^{-3} radians) and an oscillation frequency of 1 Hz.

2.4. Cell Culture. Cell viability was studied by culturing H9c2 cardiac myoblasts (ATCC, Manassas, VA) onto the surfaces of polymeric films following similar procedures in the literature.[54−57] The films were prepared by dissolving the polymer in THF, followed by applying a small quantity of the solution onto a glass petridish and, then drying in ambient. Cells were expanded in T-125 flasks, supplemented with Dulbecco's modified Eagles medium (ATCC, Manassas, VA), 10% fetal bovine serum (Invitrogen, Carlsbad, CA), and 0.01% penicillin/streptomycin. Once confluent, the ninth passage cells were cleaned with phosphate buffered saline, trypsinized, and centrifuged at 800 rpm for 8 min. After centrifugation, the supernatant was aspirated off and the cell pellet was resuspended in 8 mL of the aforementioned medium. Aliquot of 1 mL of medium (approximately 1 × 10^5 cells) was administered onto the polymer-coated petridishes. The cells were resupplied with fresh medium every 2 days. After 2 weeks of cells growth, pictures were taken using a Nikon phase contrast microscope.

3. Results and Discussion

3.1. Polymer Synthesis and Appearance of the Polymer. The polycondensation reaction was carried out in a nitrogen atmosphere to avoid the undesirable reaction of diorganodichlorosilane with moisture, which could affect the stoichiometry and lead to a decrease in molecular weight. A small stoichiometric excess of the silane was used to counter any traces of moisture in the reactants. The condensation

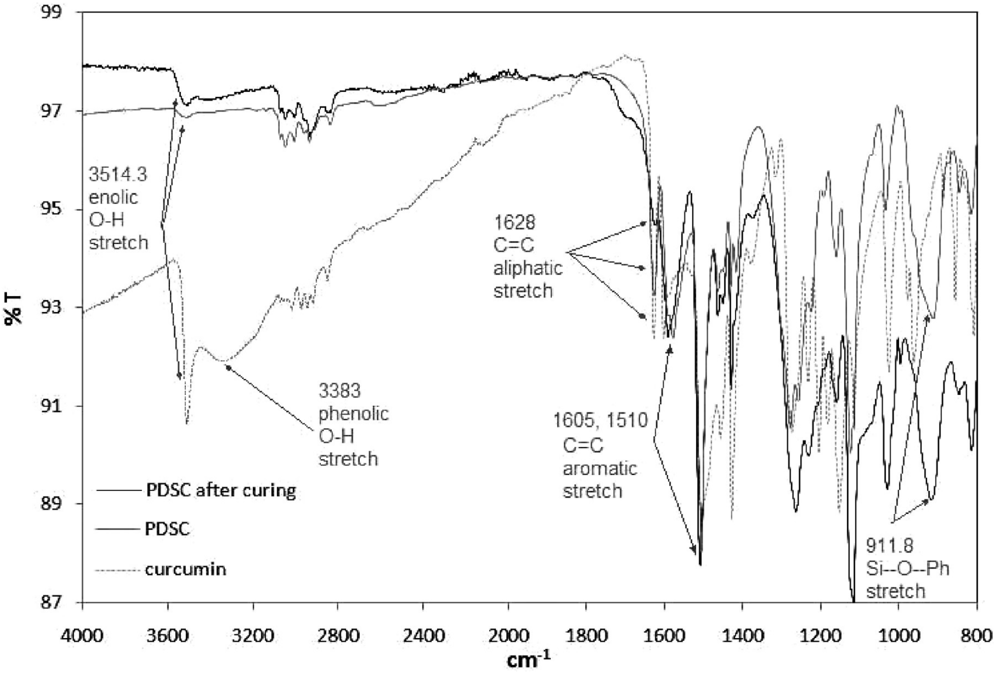


Figure 2. FTIR spectrum of poly[(arylenedioxy)(diphenylsilylene)] (PDSC) polymer before curing (gray line), after curing in a DSC pan at 270 °C for 10 min (dark line) and pure curcumin (dotted line) .

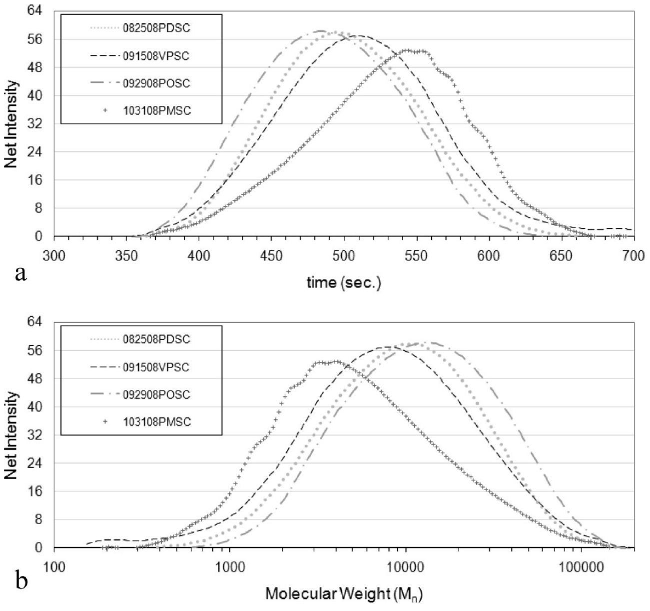


Figure 3. GPC traces of poly[(arylenedioxy)(diorganylsilylene)]s in THF, eluting at 1 mL/min: (a) plot of intensity vs time; (b) plot of intensity vs molecular weight (M_n) after calibration with polystyrene standards.

product, HCl, was removed from the polymerization system by reacting with triethylamine to form triethylamine hydrochloride salt as precipitate, which drove the equilibrium favorably to the production of polymers. The salt formation, accompanying a color change in the suspension, was indicative of the progress of polymerization reactions.

The polymer suspension was precipitated in methanol due its ability to dissolve both unreacted curcumin and the salt. The crude polymer was suspended in chloroform prior to filtration since chloroform dissolved the polymers, but the residual impurities (i.e., the salt and curcumin) were hardly soluble in chloroform.[31] Filtration also helped eliminate any possible cross-linked material produced as a result of traces of trichlorosilane in the reactant or due to trifunctionality of curcumin as a result of (silylation at the enolic OH).

The pure, methanol-precipitated polymers were obtained as a yellow powder in case of PDSC and VPSC and as an orange powder for PMSC. POSC was obtained as a brown, sticky, tar-like material. Polymer yields were in the 70−80% range, except for the significantly lower yield for the PMSC polymer (Table 1). This could be due to the relatively higher solubility of the smaller dimethylsilane ($-Si(CH_3)_2-$) unit of PMSC in methanol, which was the nonsolvent used to precipitate the crude polymer. It is likely that the lower molecular weight oligomers of PMSC were washed away in methanol, while oligomers of, say PDSC, with same number of repeat units were precipitated due to the bulky substituents on the Si atom.

3.2. Structure Characterization. The polymer structures were characterized using ^{1}HNMR, FTIR and elemental analysis. ^{1}HNMR spectra for all the polymers are shown in Figure 1 and details are tabulated in Supporting Table 1. ^{13}CNMR chemical shifts are reported in Supporting Table 2. While the few fractional components of the ^{1}HNMR integration ratios are sufficiently close to their expected nearest integer values, they arise due to the presence of end groups in the polymer.[58] The presence of an OH peak at ∼16 ppm as well as the presence of the methine proton at ∼5.8 ppm show that the β-diketone unit tends to be in the enol form. This fact is in agreement with Matsumis' work on polyesters containing curcumin in the backbone[31] and is also verified by the presence of a broad OH peak at 3514 cm^{-1} in the representative FTIR spectrum (Figure 2). The broad band in the 900−1000 cm^{-1} region corresponds to the Si−O−Ph stretching.[59] Furthermore, the %C and %H values obtained from elemental analysis match very closely to the calculated theoretical content of these elements in the backbone structure (Table 1). These results are in agreement with the targeted structures of the repeat units in the polymers as shown in Scheme 1.

3.3. Determination of Molecular Weight. The GPC traces of the polymers are shown as plots of intensity against elution time in Figure 3a. The traces are replotted as intensity vs molecular weight after calibration with the polystyrene standards in Figure 3.b. The plots appear to be in the shape of bell curves with polydispersity index (PDI) values between 2 and 3, which is typical of step growth polymerization.[60] As summarized in Table 1, these polymers have M_n values in the 10,000 to 20,000 range. PMSC has the lowest M_n value, which is understandable since the pendant methyl groups on the Si atom have much lower molecular weight than, for example, the n-octyl groups of PDSC.

3.4. TGA Measurements. The TGA curves of these curcumin-based polymers, measured in air and in nitrogen are presented in Figure 4 and Figure 5, respectively. The one percent weight loss temperature is considered a good indication of thermo−oxidative stability of polymers and is representative of the temperature at the onset of degradation.[61−63] From a processing standpoint, polymers are typically heated to 20−30 °C below this degradation temperature. The TGA results indicate that all these polymers are stable at 250 °C in air and at 280 °C in nitrogen (Table 2). Also, the residual SiO_2 contents after heating the samples to 850 °C in air are close to the theoretical SiO_2 contents calculated from the monomer feeds (Table 2).

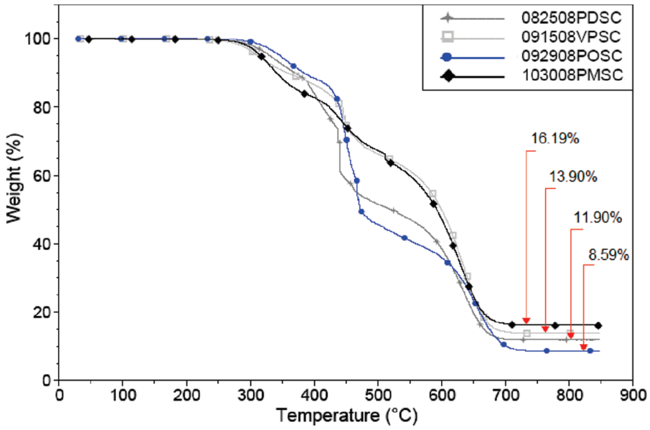


Figure 4. TGA curves of poly[(arylenedioxy)(diorganylsilylene)]s heated at 10 °C/min in air.

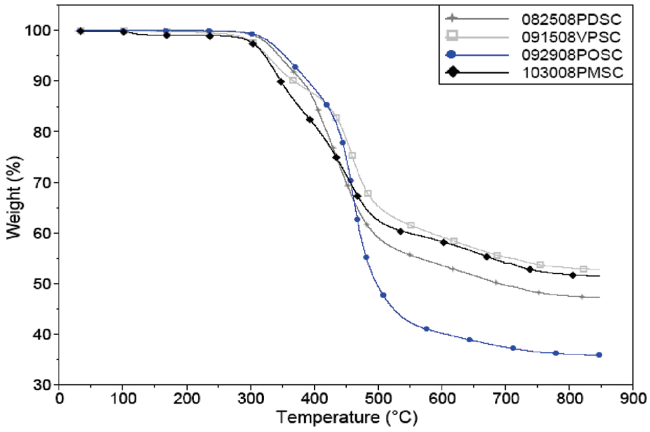


Figure 5. TGA curves of poly[(arylenedioxy)(diorganylsilylene)]s heated at 10 °C/min in nitrogen.

3.5. DSC Measurements. The presence of Si−O bonds in a repeat unit of the polymer backbone imparts a highly amorphous character to the polymers as is evident from the presence of a readily identifiable glass transition (T_g) and the absence of a clear melting temperature (T_m). The T_g values vary from as low as 23.8 °C for POSC to as high as 131.4 °C for PDSC. The low T_g for the polymers containing alkyl, e.g., *n*-octyl, groups is anticipated because such a long pendant side-chain should increase the polymer chain segmental motions. This also suggests that by changing the alkyl (or aryl) groups of the dichlorosilane reactant one can control the T_g of these materials.

In addition to the phenolic group, curcumin also lends itself to polymerization via the vinylene (i.e., C═C) groups present in the β-diketone unit. Upon heating to above 250 °C for the first time, the onset of a significant exothermic peak can be observed in the DSC curves (Figure 6). This could be attributed to the curing of vinylene groups. As expected, the magnitude of this peak is the greatest for the VPSC polymer, as it has an extra vinyl pendant group in addition to those in the backbone from curcumin. A high temperature DSC scan of PDSC actually reveals two exotherms (Figure 7). The first, in the 240 to 350 °C range, may be attributed to the heat generated from the thermally initiated free radical polymerization (curing) of C═C double bonds. The second, above 350 °C, has a much greater magnitude and is associated with the thermal degradation of the polymer at elevated temperature. Degradation was confirmed by visual inspection of the DSC pan, which was found to contain a large amount of ash.

The attribution of the first exotherm to thermal crosslinking or curing rather than degradation can be verified by the following experimental observations. First, the TGA measurements show that the polymers degrade well above 250 °C in a N_2 atmosphere (i.e., onset at ca. 300 °C, Table 2, fifth column). Second, the T_g value either increases by about 10 °C or completely disappears (VPSC) in the second heating curve. This is indicative of curing. In Figure 2, a comparison of FTIR spectra of PDSC polymer before and after thermal treatment (curing) in a DSC pan at 270 °C for 10 min clearly shows a decrease in the vinyl C═C peak at 1628 cm^{-1} for the cured sample. Furthermore, the samples collected from the DSC runs were put in vials with ~3 mL of THF. After 1 week, these samples had not dissolved in the solvent. This illustrates that curing had occurred to a sufficient extent to render the cross-linked material insoluble in a good solvent. Finally, the rheological measurements also support the formation of polymer networks as described below.

3.6. Rheology and Processing Considerations. A common method to characterize thermoset curing is to perform

Table 2. Thermal Properties of Poly[(arylenedioxy)(diorganylsilylene)]s: Results of TGA and DSC Measurements

					SiO_2 content	
sample	T_g (°C)[a]	T_g (°C)[b]	1% weight loss temp. in air (°C)	1% weight loss temp. in N_2 (°C)	theoretical	experimental
PDSC	131	141	285	306	10.95	11.9
VPSC	102	N/A	268	283	12.05	13.9
PMSC	95	113	280	295	14.15	16.2
POSC	24	N/A	305	312	9.68	8.6

[a] Determined as the point of inflection (i.e., peak in derivative) of the first heating cycle. [b] Determined as the inflection of the second heating cycle (measured on selected samples for confirmation purpose).

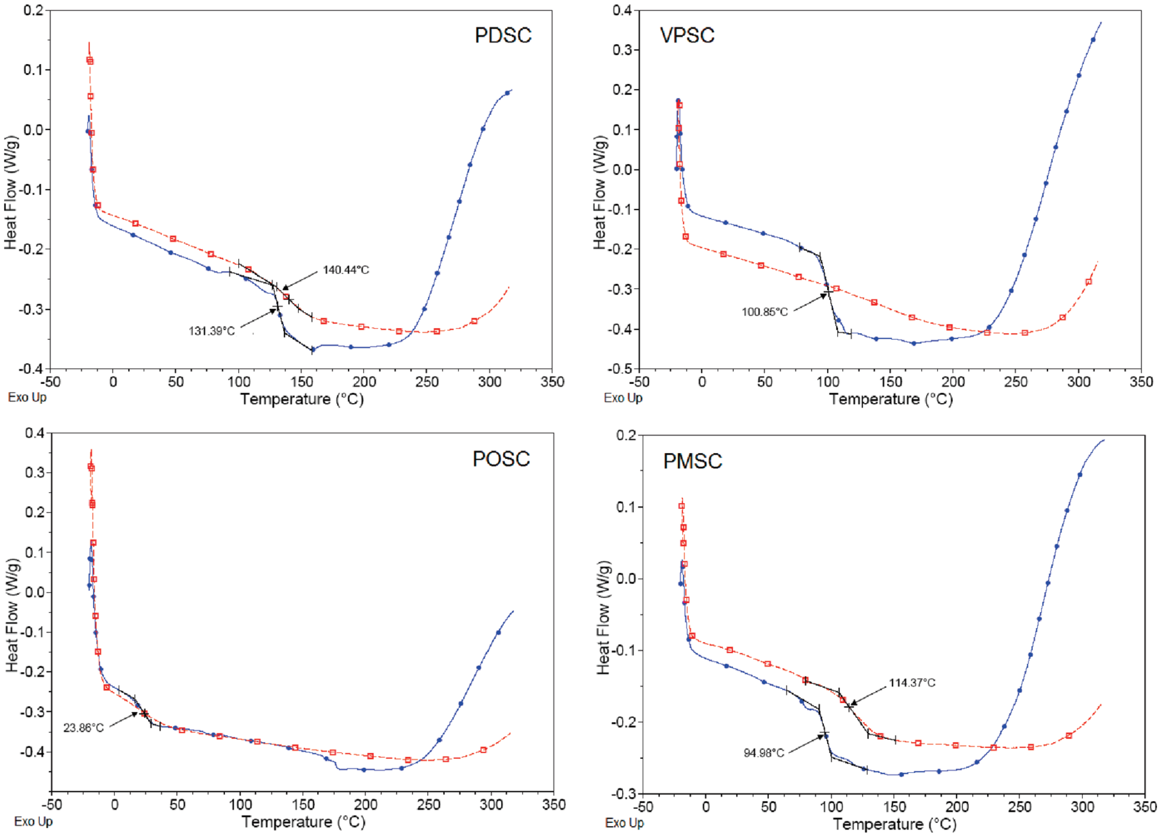


Figure 6. DSC isotherms of poly[(arylenedioxy)(diorganylsilylene)]s measured with a 15 °C/min heat−cool−heat cycle in nitrogen: (●) first heat; (☐) second heat.

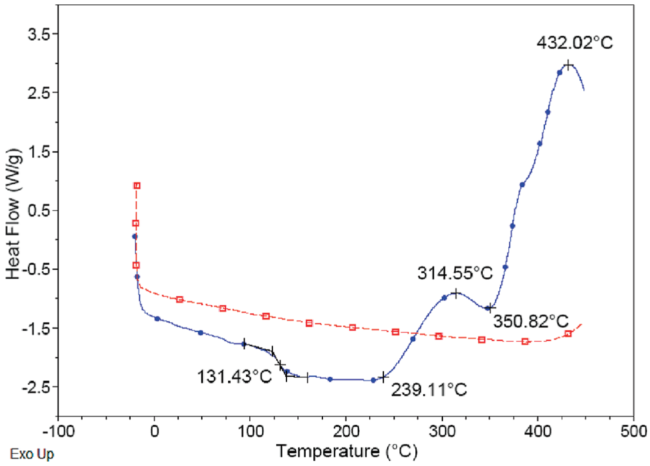


Figure 7. DSC isotherm after heating PDSC to 450 °C in nitrogen. Large exotherm due to polymer degradation is observable in the 350−430 °C range.

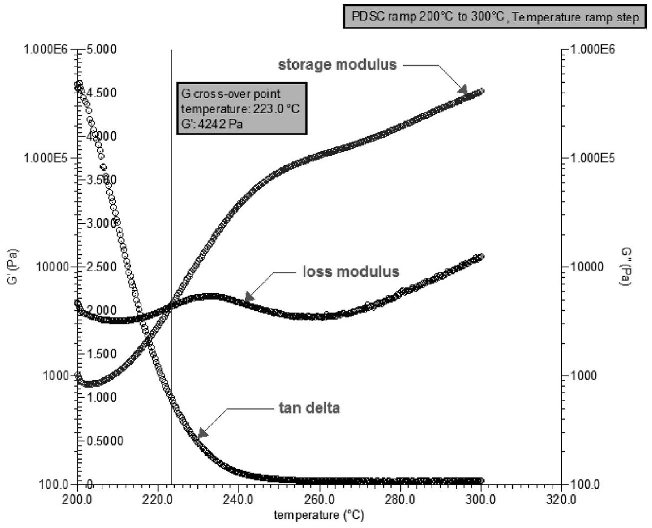


Figure 8. Plot of shear modulus vs temperature of PDSC.

parallel plate rheometry to track changes in storage modulus (G') and loss modulus (G'') of the melt as a function of time or temperature.[64] In order to determine the temperature range for effective curing of the curcumin-based polymers, a temperature scan was performed to monitor changes in G' and G'' as a function of temperature. A typical scan is shown in Figure 8 for PDSC. As the temperature increased, there was a crossover point between the storage and loss moduli at 223 °C ($G' \sim 4200$ Pa). At the start of the temperature scan, the polymer melt typically does not have a network structure and exhibits significant damping. This results in a loss modulus G'', which is larger than the storage modulus G' ($\tan \delta > 1$). The crossover point, where G' becomes the same as G'', is taken as the gel point, where the polymer network structure has developed sufficiently to exhibit pseudoelastic properties.[65]

For optimum processability, one would prefer to have sufficient time to process the material prior to the gel point. Since the thermal curing of the curcumin-based polymers should be chemical reactions among C=C double bonds with a rate that increases with temperature, performing the processing at temperatures below 223 °C should result in slower curing of the material, which in turn would allow for

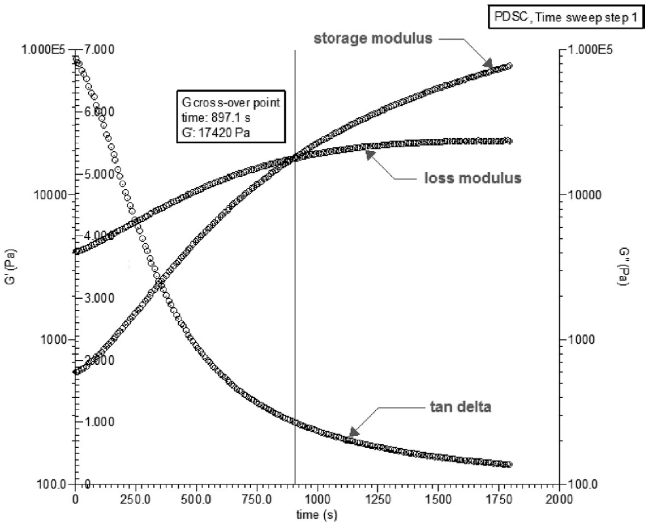


Figure 9. Plot of shear modulus vs time of PDSC.

processing over a longer period of time. Such a longer time (or wider processing window) is generally desired in the processing. The opening of the processing window was confirmed by the results seen in a time sweep performed at a constant temperature of 200 °C (Figure 9). These results indicate that one would have roughly 900 s (15 min) at 200 °C to process the material prior to passing the point of critical network formation/solidification. For comparison, commercial PEEK polymer tested under identical conditions had a viscosity minimum of ~250 000 Pa s, while our material had a viscosity of ~12 000 Pa s. Therefore, this material should be melt processable, with a relatively low viscosity and at least a 15 min processing window prior to curing. The insolubility of these polymers after thermal cycling (section 3.5) above cure temperatures is also consistent with the development of a cross-linked network structure. Further investigation is in progress to establish the relationship between the processing conditions and the structures of the curcumin-based polymers for future manufacturing of biodevices.

3.7. Cell Proliferation. Cell proliferation was examined via phase contrast microscope, after 2 weeks of cell maintenance on the four curcumin-based polymeric films. After 2 weeks of culturing the control group without the polymer coating, cardiac myoblasts of typical phenotype were generated, which can be seen in the phase contrast image of the control group (Figure 10a). While two of the polymeric films were found to support cellular life after 2 weeks of cell maintenance, the others did not support cell adhesion. PDSC supported myoblast growth and proliferation. Figure 10b is a phase contrast microscope image of cell growth on the PDSC film. According to the figure, the cell density on the PDSC films far exceeds that of the control group, while the phenotype appears to be the same. In addition to the PDSC film, the POSC films were also found to support H9c2 cell growth. One of the most interesting observations about the cell growth on the POSC film is the change in phenotype of the cells. These differences can be seen in Figure 10c; not only is the cell density greater than that of the control group, but many of the cells have a very elongated structure, resembling that of neuronal cells. The reason for such a change in phonotype is not yet understood. Similar methods (but with more quantitative studies) have been used by other researchers to establish biocompatibility of different polymeric materials.[56,57] These preliminary results indicate that the PDSC and POSC materials are non-toxic to myoblast cells and therefore have the potential to be used as implant materials or biocompatible scaffolds for *in vitro* testing. However, it must be noted that these cell proliferation results are only preliminary. More rigorous biological characterization is currently under progress and will be reported in a future publication which addresses the biological compatibility of these materials.

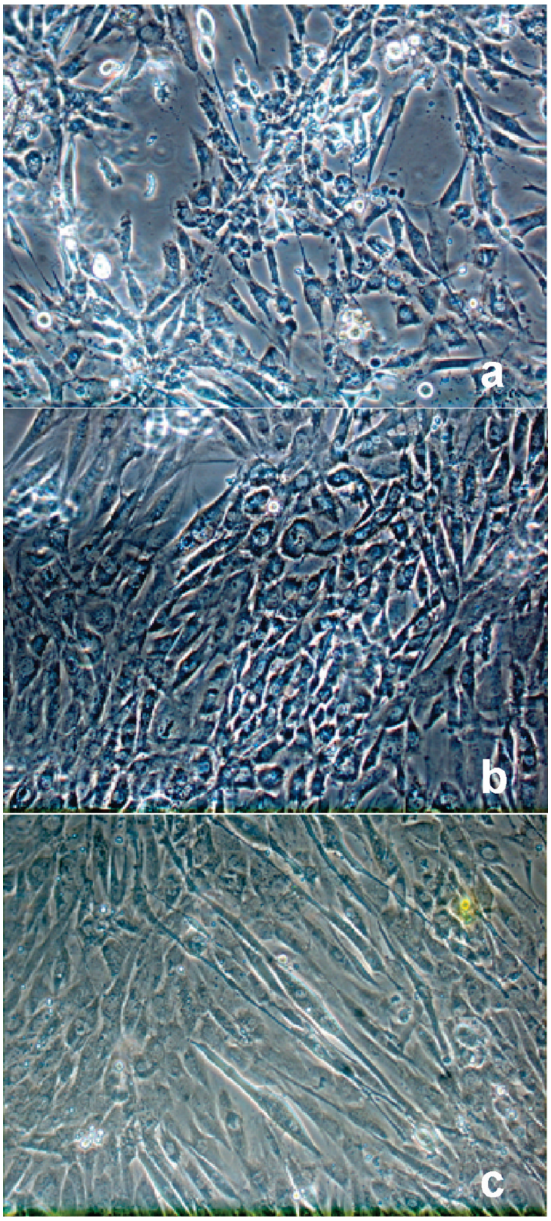


Figure 10. (a) H9c2 cardiac myoblasts cultured on the standard polystrene Petri dish (control group). (b) H9c2 cells growthing on a PDSC film after 2 weeks of cell maintenance. (c) H9c2 cells growing on a POSC film after 2 weeks.

4. Conclusion

We have demonstrated, for the first time, the synthesis of a series of poly[(arylenedioxy)(diorganylsilylene)]s via polycondensation reaction between curcumin and diorganodichlorosilanes. The materials had high molecular weight and good thermal stability. The polymers with pendant phenyl and *n*-octyl groups supported cellular life which suggests potential for use as scaffold materials.

The T_g of these polymers is dependent on the pendant organic group of the diorganodichlorosilanes. Such a tunability of T_g

could be exploited to produce polymers of desired mechanical properties. The presence of the vinylene groups in the β-diketone unit of curcumin allows an option of thermally cross-linking these materials to prepare rigid thermoset networks. This offers the opportunity of injecting a low viscosity polymer melt into a heated mold where it cures over time, resulting in a cross-linked biomaterial in a reactive injection molding process.

These novel polymers represent a new class of bio-based polymers with one monomer being obtainable from a renewable plant source. Further investigations regarding the biocompatibility, possible anti-inflammatory and other biomedical effects and mechanical properties of these materials are in active progress and the results will be presented in our future articles.

Acknowledgment. We thank Greene Tweed & Co. for supporting this work. Y.W. is grateful to Chung Yuan Christian University for the honor of a Chair Professorship in Chemistry and Nanotechnology.

Supporting Information Available: Supporting Table 1, containing ^{1}HNMR chemical shifts, peak assignments and integration ratios for PDSC, VPSC, PMSC, and POSC, and Supporting Table 2, containing ^{13}CNMR shifts and intensities for the same polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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