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# Hybrid Sol–Gel Glasses with Glass-Transition Temperatures Below Room Temperature

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Melting gels are hybrid gels that have the ability to soften and flow at around 100°C for some combinations of mono- and di-substituted alkoxyloxanes, where substitutions are either all aromatic or all aliphatic. In this study, melting gels were prepared using phenyltriethoxysilane (PhTES) and dimethyldiethoxysilane (DMDES), meaning both an aromatic and aliphatic substitution. Differential scanning calorimetry was performed to identify glass-transition temperatures, and thermal gravimetric analysis coupled with differential thermal analysis (TGA-DTA) was performed to measure weight loss. The glass-transition temperatures ( $T_g$ ) ranged from  $-61^\circ\text{C}$  to  $+5.6^\circ\text{C}$ , which are between the values in the methyl only system, where all  $T_g$  values are less than  $0^\circ\text{C}$ , and those values in the phenyl only system, where  $T_g$  values are greater than  $0^\circ\text{C}$ . The  $T_g$  decreased with an increase in the DMDES fraction. Below  $450^\circ\text{C}$ , the gels lost little weight, but around  $600^\circ\text{C}$  there was a drop in weight. This temperature is lower than the temperature for gels prepared with only aromatic substitutions, but higher than that for gels prepared with only aliphatic substitutions. Final heat treatment was carried out at  $150^\circ\text{C}$  for the gel with 80%PhTES-20%DMDES (in mol%), and the consolidation temperature increased with increasing DMDES content to  $205^\circ\text{C}$  for the gel with 50%PhTES-50%DMDES. After this heat treatment, the melting gels no longer soften.

## I. Introduction

PREVIOUSLY, melting gels were prepared from mixtures of mono-substituted and di-substituted alkoxyloxanes, where the substitutions were all aromatic groups<sup>1</sup> or all aliphatic.<sup>2</sup> Varying the ratios of mono- and di-substituted alkoxyloxanes led to changes in the glass-transition temperature ( $T_g$ ) and the consolidation temperature ( $T_{\text{con}}$ ), as well as the separation of these temperatures. In an effort to control the temperature range between  $T_g$  and  $T_{\text{con}}$ , it would be interesting to see if mixtures of aliphatic and aromatic substitutions can be made to cover temperature ranges not available with only one or the other. The range between  $T_g$  and  $T_{\text{con}}$  is important for applications involving pattern transfer and imprinting.<sup>3,4</sup>

Melting gels belong to the category of hybrid gels that contain a direct bond between the inorganic component and organic groups,  $\text{R}_x\text{Si}(\text{OR}')_{4-x}$ . One example of this kind of precursor is phenyltriethoxysilane (PhTES). By hydrolysis-

polycondensation of this precursor, an inorganic network grafted with phenyl groups can be obtained. The Si–C bonds are not affected by the sol–gel processes.<sup>5,6</sup> The functionality of these precursors decreases with the increasing number of the organic groups bonded directly to the silicon atom.<sup>7</sup> In addition, the increase in the number of organic groups has the consequence of decreasing the degree of cross-linking of the inorganic network. For example, dimethyldiethoxysilane (DMDES) after hydrolysis-polycondensation forms polydimethylsiloxane (PDMS). Structural studies using  $^{29}\text{Si}$  NMR<sup>8,9</sup> showed that PDMS contains linear molecular chains. However, when DMDES is mixed with alkoxyloxanes with higher functionality, such as methyltriethoxysilane (MTES)<sup>2</sup> or tetraethoxysilane (TEOS),<sup>10</sup> it is possible to form cross-linked siloxanes with variable density, flexibility, and hydrophobicity.<sup>11</sup>

Using  $^{29}\text{Si}$  NMR, Monredon-Senani et al.<sup>12</sup> found that the silica surface was covalently grafted with methyl groups, when using MTES or DMDES, which increased the hydrophobicity of the silica surface. Bennevault-Celton et al.<sup>13</sup> showed that DMDES along with aminoalkylaloxysilane were used to preserve the flexibility of aging cellulosic paper in items of cultural heritage. Weiser et al. used TEOS and DMDES<sup>14</sup> to incorporate Lipase AK in a sol–gel procedure to enhance its thermal stability and long-term operational stability.

As DMDES reacts to form only linear chains of PDMS, it can be used to prepare hollow hybrid silica spheres by emulsion templating.<sup>15,16</sup> The basic idea is to prepare highly uniform silicone oil-in-water emulsion droplets by hydrolysis and polycondensation of DMDES. These droplets are further used as a template for silica deposition by hydrolysis of TEOS<sup>15</sup> or polydopamine.<sup>16</sup> These hollow nanoparticles can be used for drug carriers.

Kuniyoshi et al.<sup>17</sup> investigated the initial hydrolysis-polycondensation of PhTES in an acid medium using  $^{29}\text{Si}$  NMR and gel permeation chromatography (GPC). They demonstrated that hydrolysis and polycondensation proceeded simultaneously in the presence of hydrochloric acid. In contrast, hydrolysis went to completion before polycondensation when acetic acid was used as a catalyst. In addition, it was shown that the polycondensation rate could be controlled by changing the reaction temperature. Katayama et al.<sup>18</sup> studied the catalytic effect of  $\text{Al}(\text{O}-\text{sec}-\text{C}_4\text{H}_9)_3$ ,  $\text{Ti}(\text{O}-\text{iso}-\text{C}_3\text{H}_7)_4$  and  $\text{Nb}(\text{OC}_2\text{H}_5)_5$  on the hydrolysis and polycondensation of PhTES and MTES. Using  $^{29}\text{Si}$ -NMR and GPC, they determined that reaction of PhTES is promoted by these catalysts, and the catalytic effect increases in the order of decreasing valence  $\text{Nb} < \text{Ti} < \text{Al}$ .

The binary system PhTEOS-DMDES was investigated for preparation of microlens arrays by molding a film on a template.<sup>19</sup> Using the same system, Katayama et al.<sup>20</sup> designed

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organosiloxanes for low friction materials under fluid lubrication conditions. The coatings obtained in this system have good wettability with oil up to 400°C.

Matsuda et al.<sup>21</sup> were the first to call hybrid gels that softened “melting gels”, when they prepared poly(benzylsilsesquioxane) particles, which were then deposited on an ITO substrate by electrophoretic deposition. After heat treatment, continuous thick transparent films were obtained. Later, using the pairs PhTES and DPhDES or MTES and DMDES in two steps of catalysis, Masai et al.<sup>22</sup> obtained organically modified polysilsesquioxanes with a low softening point. In the first step, they used hydrochloric acid, as a catalyst, followed by ammonia in the second step for condensation. <sup>29</sup>Si-NMR and GPC were used to study the complex structure of the gels in the PhTES-DPhDES and (PhTES)<sub>1</sub>(MTES)<sub>(1-x)</sub>-DPhDES systems,<sup>23,24</sup> which showed that the molecular structures of the gels were three dimensional, with the organic groups having weak bonds between molecular chains.

Previously, the thermal behavior of melting gels in the MTES-DMDES system was studied.<sup>25</sup> It was found that these gels have glass-transition temperatures below 0°C, which makes them suitable for imprint lithography.<sup>26</sup> Another application for these melting gels was for hermetic barriers for electronic materials.<sup>27,28</sup> For this application it was demonstrated that the hybrid glasses obtained by consolidation of the melting gels were hydrophobic ( $\theta > 90^\circ$ ), non-porous, and had a helium transmission rate of  $\sim 8.6 \times 10^{-5} \text{ cm}^3/\text{m}^2 \times \text{day}$ .<sup>27</sup> Moreover the properties of these gels can be controlled by the systematic variation of the ratios of mono- and di-substituted precursors and by the use of aliphatic versus aromatic substitutions.<sup>7</sup>

Hybrid glasses obtained after consolidation may be a replacement for epoxies in microelectronic packaging.<sup>29</sup> The dielectric constant, as determined using impedance spectrometry, was lowest, around 3.3, in the 50% MTES–50% DMDES composition at frequencies greater than 1 kHz. As direct Si–C bonds are less polarizable than Si–O–Si, the di-substituted alkoxy silane, DMDES, contributes to decreasing the dielectric constant.

In this study, a mixture of two substituents, one aromatic and one aliphatic was investigated. PhTES is the mono-substituted precursor, and DMDES is the di-substituted precursor. The thermal behavior of the melting gels was evaluated using thermogravimetric analysis coupled with differential thermal analysis and different scanning calorimetry (DSC). After consolidation, the hybrid glasses were characterized using FT-IR and Raman spectroscopy.

## II. Experimental Procedure

### (1) Gel Preparation

The phenyl-methyl “melting gels” were obtained using a mono- and a di-substituted alkoxy silane. The mono-substituted alkoxy silane was PhTES (98% purity, Gelest Inc., Morrisville, PA). The di-substituted alkoxy silane was DMDES (97% purity, Sigma-Aldrich, Milwaukee, WI). The precursors were used without further purification. Hydrochloric acid 0.1M (Fisher Scientific, Pittsburgh, PA) was used as a catalyst. The solvent was anhydrous ethanol (Sigma-Aldrich). The mole ratio, and mole percentages for PhTES and DMDES are listed in Table I, along with the results of the thermal analysis, the time-to-gel and melting gel sample size.

A two-step synthesis was used. This two-step procedure was used before for studying the formation of the melting gels with PhTES and diphenyldiethoxysilane (DPhDES).<sup>1</sup> First the mono-substituted alkoxy silane (PhTES) was mixed with water in which the pH was adjusted to pH = 2.5 using a 0.1M HCl solution. The molar ratio PhTES to H<sub>2</sub>O was 1:1.5. After the water was added to the PhTES, the mixture was stirred continuously at 40°C in an oven in a sealed bea-

**Table I. Compositions, Glass-Transition ( $T_g$ ), Consolidation Temperature ( $T_{CON}$ ), Total Thermogravimetric Mass Loss, Time-to-gel, and Sample Volume**

PhTES/ DMDES	PhTES/ DMDES	$T_g$	$T_{CON}$	Total Mass	Time-to- Gel hours	Sample Volume mL
in mol%	in mole ratio	°C	°C	Loss%		
50/50	1.0/1.0	-61.0	205	65	72	0.21
57/43	1.0/0.75	-55.7	195	62	60	0.20
66/34	1.0/0.50	-29.6	180	58	36	0.19
74/26	1.0/0.35	5.6	160	53	24	0.27
80/20	1.0/0.25	2.1	150	55	24	0.25
100/0	1.0/0.0	33.1	130	57	24	—

ker with Parafilm®. For all compositions listed in Table I, the PhTES-H<sub>2</sub>O mixture was stirred continuously for 6 h at 40°C.

In the second step, the di-substituted alkoxy silane DMDES was diluted with absolute ethanol. The molar ratio was 4 mol alcohol to 1 mol of DMDES. The di-substituted alkoxy silane–alcohol mixture was added dropwise to the clear solution of mono-substituted alkoxy silane and water. This took about 10 min. This mixture was continuously stirred for another 2 h in a sealed beaker at 40°C. Then, the clear solution was cooled to room temperature and stirred in an open system until gelation occurred. The time-to-gel is given in Table I. The gels were then dried at 70°C for 24 h to remove residual ethanol, followed by heat treatment in ambient air at 110°C to remove the unreacted water. After these heat treatments, the gels were solid at room temperature, but they re-softened at  $\sim 100^\circ\text{C}$ .

Low viscosity gels were obtained by heating the melting gels at 100°C for 30 min. Coatings were deposited by pouring softened gels onto mica and polycarbonate substrates. Square (15 mm × 15 mm) mica plates (Grade V-4 muscovite, SPI Co., West Chester, PA) were used. The melting gel was poured onto the substrate, and the sample volume is listed in Table I. Following deposition, the coatings were treated at the consolidation temperatures listed in Table I for 24 h. The consolidation temperature was found by subjecting the samples to higher and higher temperatures, until a temperature was reached where the samples failed to soften.

## III. Materials Characterization

The thermal behavior of the fresh gels before their consolidation was studied using differential thermal analysis (Perkin-Elmer DTA-7, Shelton, CT), thermogravimetric analysis (Perkin-Elmer TGA-7) and differential scanning calorimetry (DSC TA-Q-2000, New Castle, DE). DTA and TGA were recorded with a heating rate of 5°C/min in the temperature range between 50°C–800°C under air flow (20 mL/min). The DSC analyses were recorded using a 5°C/min heating rate between -70°C and 400°C under nitrogen flow (20 mL/min).

The DSC isothermal hold experiments were performed by heating the fresh samples at 5°C/min from room temperature to the consolidation temperature. At this temperature, the sample was held isothermally for 2 h, followed by cooling to -70°C. Then the DSC analysis was performed again in a dynamic mode from -70°C up to 400°C with a heating rate of 5°C/min, same as the original heating rate.

The FT-IR spectra were recorded between 600–4000 cm<sup>-1</sup> using ThermoNicolet Avatar 360 FTIR (Waltham, MA) equipped with a Smart Endurance ATR attachment (diamond crystal). The resolution for the FTIR was 2 cm<sup>-1</sup> and 100 spectra were averaged. The spectra were acquired under a Leica (Buffalo Grove, IL) optical microscope at 50× magnification and were recorded at fourteen different points along a line of 100 μm. Raman spectra analysis was performed using a Renishaw® in Via Raman Microscope

(Renishaw, Gloucestershire, UK) equipped with a 765 nm laser. The Raman spectra were recorded between 100–4000  $\text{cm}^{-1}$ . The resolution for the Raman was 0.5  $\text{cm}^{-1}$ .

Contact angles were measured on samples that had been fully consolidated for 24 h at their indicated consolidation temperatures. The contact angle  $\theta^\circ$  was measured using a T-200 basic Theta Optical Tensiometer (Biolin Scientific, Stockholm, Sweden) equipped with LED blue light source and with a standard 60 fps camera with a special zoom lens. For each sample ten measurements of the contact angle were acquired and the data were averaged. The contact angle data were analyzed using Pendant Drop Surface Tension Software 3.80 (Biolin Scientific). Measurement was made at room temperature. All contact angles were greater than  $90^\circ$ , and are not reported individually.

#### IV. Results

The compositions for melting gels in the PhTES-DMDES system are listed in Table I, along with information on pure PhTES.<sup>17</sup> During the synthesis, the initial mixture of PhTES and water is immiscible, but after 5 h of continuous stirring at  $40^\circ\text{C}$ , the ethanol released by the polycondensation reaction<sup>17</sup> produces a solution. The temperatures of consolidation are listed also in Table I, and they vary from  $150^\circ\text{C}$  to  $205^\circ\text{C}$  as the concentration of di-substituted alkoxy silane DMDES is increased.

The TGA results are shown in Fig. 1. The total weight loss is included in Table I. The weight loss generally increases with an increase in the concentration of DMDES, with the exception of sample 74% PhTES-26% DMDES. This sample has the lowest weight loss 53%, which is slightly lower than that for 80% PhTES-20% DMDES, and both are lower than 100% PhTES. Otherwise, there is little weight loss below  $200^\circ\text{C}$ . Between  $200^\circ\text{C}$  and  $330^\circ\text{C}$ , there is noticeable weight loss, which is greater in samples with higher concentrations of DMDES. There is a plateau between  $330^\circ\text{C}$  and  $450^\circ\text{C}$ . Between  $450^\circ\text{C}$  and  $650^\circ\text{C}$ , there is a second

weight loss in all samples, with the greater amounts occurring in samples with higher concentrations of PhTES.

In comparing the TGA and the DTA plots of Fig. 1, the first weight loss on the TGA plot is accompanied by a small exotherm at  $310^\circ\text{C}$ . The exotherm is more noticeable for the samples with higher concentration of DMDES, indicating that this is oxidation of some unreacted ethoxy groups. The second weight loss is the main decomposition step. This is accompanied by a large asymmetrical exotherm between  $460^\circ\text{C}$  and  $600^\circ\text{C}$ . Around  $460\text{--}490^\circ\text{C}$ , there is a small exotherm associated with oxidation of remaining methyl groups. This exotherm is less prominent in samples with more PhTES. An exotherm at  $440^\circ\text{C}$  was prominent in the MTES-DMDES system.<sup>27</sup> For samples with more PhTES, the exotherm is more centered around  $600^\circ\text{C}$ , where remaining phenyl groups oxidize. All weight loss occurs by  $650^\circ\text{C}$ .

The DSC curves for all five compositions are displayed in Fig. 2, recorded during constant rate heating in nitrogen flow. The inflection points at the low temperature end are noted, and the glass-transition temperatures, estimated in the usual way by using the intersection of tangents, are listed in Table I. The curves for the lowest glass transitions are less reliable because of the lower temperature limit of  $-70^\circ\text{C}$  for the DSC. The exotherm around  $315^\circ\text{C}$  is in good agreement with the exotherm found on the DTA plots for decomposition of the ethoxy groups. There is also an endotherm around  $220^\circ\text{C}$  for samples with large amounts of DMDES, which may indicate reactions with hydroxyls. This endotherm is not seen in DTA, because DTA is carried out in air.

As listed in Table I, the glass-transition temperatures increase from  $-61.0^\circ\text{C}$  to  $5.6^\circ\text{C}$  as PhTES increases. The sample with composition 74% PhTES-26% DMDES has the highest glass-transition temperature, slightly higher than that for 80% PhTES-20% DMDES. The value for pure PhTES is  $33.1^\circ\text{C}$ .<sup>17</sup>

In Fig. 3 the DSC curves for the sample 66% PhTES-34% DMDES are shown during the initial heating of a fresh gel (1), during an isothermal treatment of a fresh gel (2) and

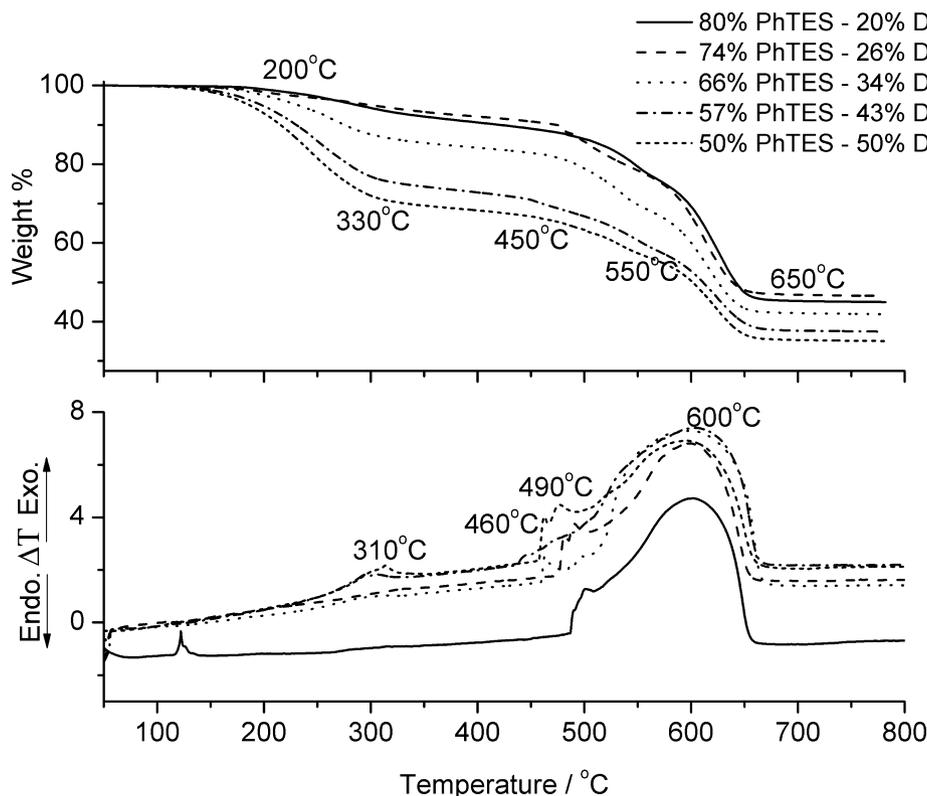


Fig. 1. Thermogravimetric (TG) curves and differential thermal analysis (DTA) curves for the fresh melting gels recorded under oxidative condition.

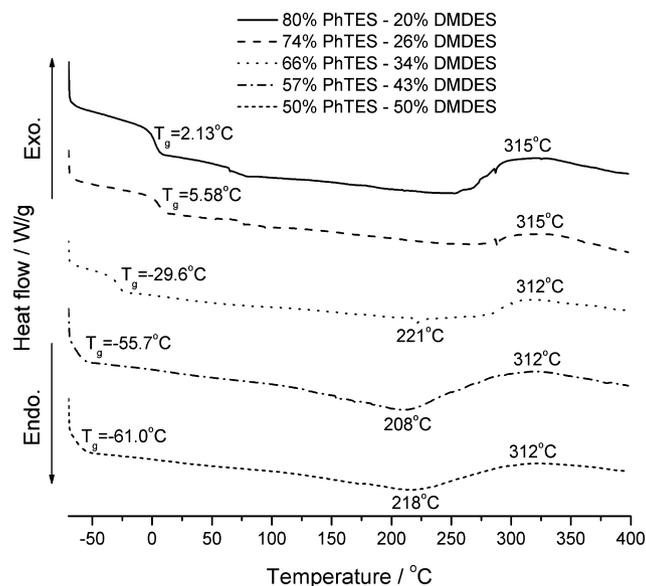


Fig. 2. Differential scanning calorimetry (DSC) curves for fresh melting gels heated under nitrogen.

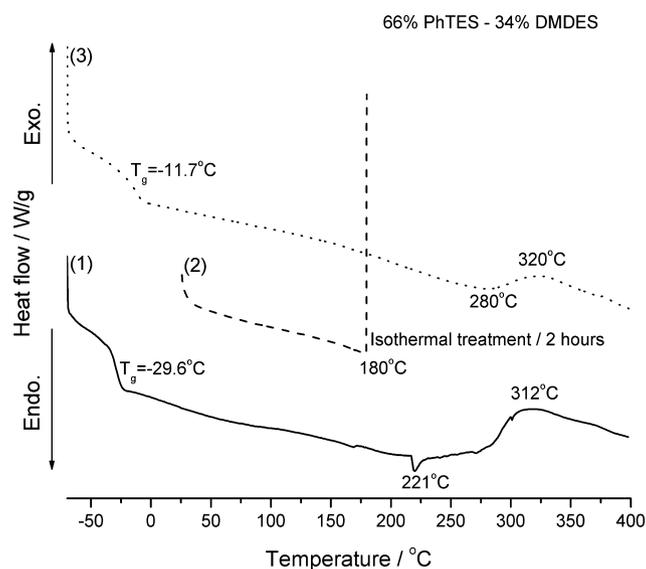


Fig. 3. DSC curves for the melting gels with composition 66% PhTES-34% DMEDES - (1) fresh melting gel heated from  $-70^{\circ}\text{C}$  to  $400^{\circ}\text{C}$  at  $5^{\circ}\text{C}/\text{min}$ ; (2) held isothermally for 2 h at the consolidation temperature  $180^{\circ}\text{C}$ ; (3) reheated from  $-70^{\circ}\text{C}$  to  $400^{\circ}\text{C}$  at  $5^{\circ}\text{C}/\text{min}$  after isothermal consolidation.

following the isothermal treatment (3). The purpose of the isothermal experiments was to investigate what happens at the consolidation temperature. Initially, the sample, indicated by curve (2), was heated at  $5^{\circ}\text{C}/\text{min}$  from room temperature up to the consolidation temperature  $180^{\circ}\text{C}$ . Then the sample was held there for two hours, after which the sample was cooled down to  $-70^{\circ}\text{C}$ . Finally, the sample was heated from  $-70^{\circ}\text{C}$  to  $400^{\circ}\text{C}$ , again at  $5^{\circ}\text{C}/\text{min}$ . After the isothermal treatment, the endotherm at  $220^{\circ}\text{C}$  is missing, and the exotherm around  $315^{\circ}\text{C}$  is somewhat diminished. Most notably, the glass-transition temperature increases from  $-29.6^{\circ}\text{C}$  to  $-11.7^{\circ}\text{C}$ . This is a significant increase in the glass-transition temperature, indicating changes in the relaxation behavior of the melting gel structure.<sup>30</sup> Other compositions were subjected to the same type of isothermal hold at a temperature near their consolidation temperature, and similar increases in the glass-transition temperature were measured.

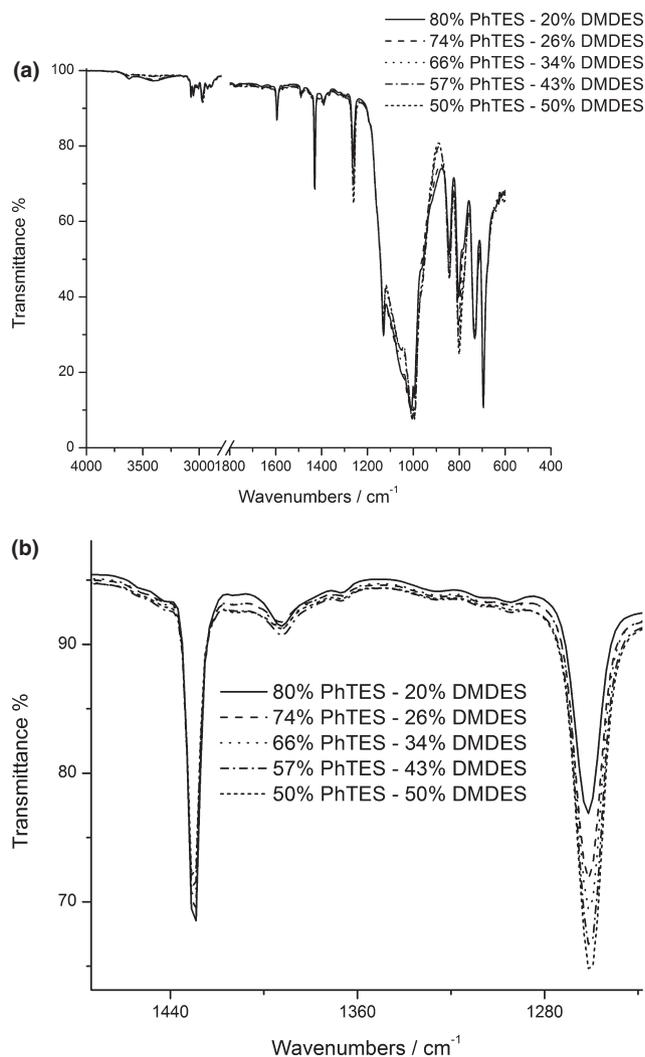


Fig. 4. The FT-IR spectra of the melting gels after their consolidation (a) a detail of the FT-IR spectra of hybrid glasses (b).

For example, the  $T_g$  increased from  $2.1^{\circ}\text{C}$  to  $18.3^{\circ}\text{C}$  for the composition with 80% PhTES-20% DMEDES.

The FT-IR spectra of all hybrid glasses following their consolidation treatments are presented in Fig. 4(a). The peak assignments are listed in Table II. The presence of methyl and phenyl groups is apparent in the hybrid glasses even after all the reactions of hydrolysis and polycondensation and also the thermal treatment. The presence of the organic groups was identified by the occurrence of the following absorption peaks:  $\nu_{\text{asym}} \text{CH}$  from  $\text{C}_6\text{H}_5$  at  $3071 \text{ cm}^{-1}$ ,  $\nu_{\text{sym}} \text{CH}$  from  $\text{C}_6\text{H}_5$  at  $3049 \text{ cm}^{-1}$ ,  $\nu_{\text{asym}} \text{CH}_3$  at  $2968 \text{ cm}^{-1}$ ,  $\nu_{\text{sym}} \text{CH}_3$  at  $2924 \text{ cm}^{-1}$ ,  $\nu \text{C-C}$  from  $\text{C}_6\text{H}_5$  at  $1428 \text{ cm}^{-1}$ ,  $\delta_{\text{sym}} \text{CH}_3$  from  $\text{Si-CH}_3$  configuration at  $1258 \text{ cm}^{-1}$ ,  $\rho \text{CH}_3$  at  $730 \text{ cm}^{-1}$ , and  $\tau \text{C-C}$  from the phenyl ring at  $695 \text{ cm}^{-1}$ .<sup>31-33</sup> There is evidence for the existence of Si-C bonds in the FT-IR spectra by the presence of the absorbance peaks at  $\nu \text{Si-C}$  from  $\text{Si-C}_6\text{H}_5$  at  $1135 \text{ cm}^{-1}$ <sup>34</sup> and  $\nu \text{Si-C}$  from  $\text{Si-CH}_3$  at  $695 \text{ cm}^{-1}$  which overlap with  $\tau \text{C-C}$  from the phenyl ring.<sup>31</sup> The characteristic vibrations indicative of the Si-O-Si bonds in the organically modified glass network are found at  $799 \text{ cm}^{-1}$  for  $\nu_{\text{sym}} \text{Si-O-Si}$ , at  $846 \text{ cm}^{-1}$  for  $\delta \text{Si-O-C}$ , at  $999 \text{ cm}^{-1}$  due to the  $\nu_{\text{asym}} \text{Si-O-Si}$  (transverse) and at  $1055 \text{ cm}^{-1}$  due to  $\nu_{\text{asym}} \text{Si-O-Si}$  (longitudinal).<sup>31,35</sup>

Figure 4(b) is an expansion of the spectral domain between  $1475$  and  $1238 \text{ cm}^{-1}$  where  $\nu \text{C-C}$  from  $\text{C}_6\text{H}_5$  and,  $\delta_s \text{CH}_3$  from  $\text{Si-CH}_3$  are present. As seen here, the intensity of the peak assigned to the  $\nu \text{C-C}$  from  $\text{C}_6\text{H}_5$  decreases as the concentration of DMEDES increases, whereas the intensity of the vibration characteristic of  $\delta_s \text{CH}_3$  from  $\text{Si-CH}_3$

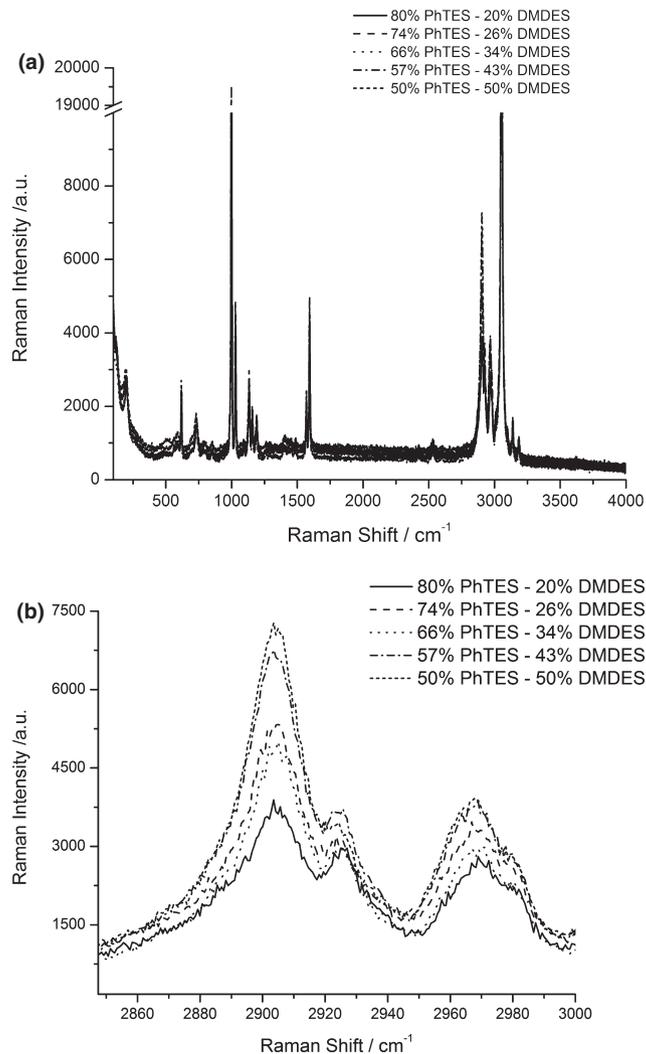
**Table II. Peak Assignments for FTIR and Raman Spectra of Melting Gels**

FTIR Wave numbers/cm <sup>-1</sup>	Raman Raman shift/cm <sup>-1</sup>	Assignments
3071 (w)	3143 (w)	$\nu_{\text{asym}} \text{CH} (\text{C}_6\text{H}_5)$
3049 (w)	2920 (s)	$\nu_{\text{sym}} \text{CH} (\text{C}_6\text{H}_5)$
2968 (w)	2972 (m)	$\nu_{\text{asym}} \text{CH}_3$
—	2925 (w)	$\nu \text{CH} (\text{CH}_2)$
2924 (w)	2900 (s)	$\nu_{\text{sym}} \text{CH}_3$
1591 (m)	—	$\gamma \text{C-H} (\text{C}_6\text{H}_5)$
—	1591 (s)	$\nu \text{C}_6\text{H}_5$
—	1571 (m)	$\nu \text{C}_6\text{H}_5$
1490 (w)	—	$\nu \text{C=C} (\text{C}_6\text{H}_5)$ aromatic ring vibration
1428 (m)	—	$\nu \text{C-C} (\text{C}_6\text{H}_5)$ aromatic ring vibration
1392 (w)	1407 (w)	$\delta_{\text{asym}} (\text{CH}_3)$
1258 (m)	1283 (w)	$\delta_{\text{s}} \text{CH}_3 (\text{Si-CH}_3)$
—	1167 (w)	Plane $\delta \text{C-H}$ deformation ( $\text{C}_6\text{H}_5$ )
1135 (s)	—	$\nu \text{Si-C} (\text{Si-C}_6\text{H}_5)$
—	1130 (m)	Plane $\delta \text{C-H}$ deformation ( $\text{C}_6\text{H}_5$ )
—	1085 (w)	$\nu_{\text{asym}} \text{Si-O-Si}$
1055 (s)	—	$\nu_{\text{asym}} \text{Si-O-Si} (\text{LO})$
—	1030 (s)	$\text{C}_6\text{H}_5$ ring deformation
999 (s)	—	$\nu_{\text{asym}} \text{Si-O-Si} (\text{TO})$
—	998 (vs)	$\text{C}_6\text{H}_5$ ring deformation
846 (m)	852 (w)	$\delta \text{Si-O-C}$
799 (s)	792 (w)	$\nu_{\text{sym}} \text{Si-O-Si}$
730 (m)	729 (m)	$\rho \text{CH}_3$
695 (s)	695 (w)	$\nu \text{Si-C} (\text{Si-CH}_3)$ overlap in FT-IR with $\tau \text{C-C}$ (phenyl ring)
—	622 (m)	$\nu \text{Si-C} (\text{Si-C}_6\text{H}_5)$
—	583 (m)	$\text{Si-O-Si}$ ring breathing vibration for 6 member
—	486 (w)	$\text{Si-O-Si}$ ring breathing vibration for a 8 member ring

increases. The general trend is an increase in the intensity of the  $\delta_{\text{s}} \text{CH}_3$  absorption in the FT-IR spectra with an increase in the number of  $\text{CH}_3$  groups.

The Raman spectra are displayed in Fig. 5(a) and the assignments are listed in Table II. The spectra contain the characteristic peaks for the phenyl and methyl groups. The presence of the phenyl groups was identified by the following vibrations:  $\nu_{\text{asym}} \text{CH}$  from  $\text{C}_6\text{H}_5$  at  $3143 \text{ cm}^{-1}$ ,  $\nu_{\text{asym}} \text{CH}$  from  $\text{C}_6\text{H}_5$  at  $2920 \text{ cm}^{-1}$ ;  $\nu \text{C}_6\text{H}_5$  characteristic for ring stretching displays a pair of peaks at  $1591$  and  $1571 \text{ cm}^{-1}$ ,  $\delta \text{CH}$  characteristic for plane deformation at  $1167$  and  $1130 \text{ cm}^{-1}$ ,  $1090$ , and  $1032 \text{ cm}^{-1}$  and the intense pairs due to  $\text{C}_6\text{H}_5$  ring deformation at  $1030$  and  $998 \text{ cm}^{-1}$ .<sup>36</sup> The presence of the methyl group was identified by the following Raman bands:  $\nu_{\text{asym}} \text{CH}_3$  at  $2972 \text{ cm}^{-1}$ ,  $\nu_{\text{sym}} \text{CH}_3$  at  $2900 \text{ cm}^{-1}$ ,  $\delta_{\text{asym}} \text{CH}_3$  at  $1407 \text{ cm}^{-1}$ ,  $\delta_{\text{sym}} \text{CH}_3$  at  $1283 \text{ cm}^{-1}$  and  $\rho \text{CH}_3$  at  $729 \text{ cm}^{-1}$ .<sup>31</sup> Characteristic bands for the silica network were the very weak peaks of  $\nu_{\text{asym}} \text{Si-O-Si}$  located at  $1085 \text{ cm}^{-1}$ ,<sup>35</sup>  $\delta_{\text{asym}} \text{Si-O-Si}$  at  $852 \text{ cm}^{-1}$ ,  $\nu_{\text{sym}} \text{Si-O-Si}$  located at  $792 \text{ cm}^{-1}$ <sup>31</sup> and  $\text{Si-O-Si}$  in plane vibration of 6 member ring and 8 member ring, respectively, identified at  $583$  and  $486 \text{ cm}^{-1}$ .<sup>37</sup> An indication of  $\text{Si-C}$ , possibly from  $\text{Si-CH}_3$ , was found as a shoulder around  $695 \text{ cm}^{-1}$ ,<sup>32</sup> whereas  $\text{Si-phenyl}$  bond was identified through the characteristic Raman vibration at  $622 \text{ cm}^{-1}$ .<sup>31,38</sup> It is clear from Fig. 5(a) that the characteristic peaks attributed to the methyl and phenyl groups have higher intensities than the peaks characteristic of the  $\text{Si-O-Si}$  backbone or  $\text{Si-C}$  bonds.

Figure 5(b) is an expansion of the Raman spectra between  $2850$  and  $3000 \text{ cm}^{-1}$ . This region of the spectrum contains the following peaks:  $\nu_{\text{asym}} \text{CH}_3$  at  $2972 \text{ cm}^{-1}$ ,  $\nu \text{C-H}$  at



**Fig. 5.** The Raman spectra of the melting gels after their consolidation (a) a detail of the Raman spectra of hybrid glasses (b).

$2925 \text{ cm}^{-1}$ , and  $\nu_{\text{sym}} \text{CH}_3$  at  $2900 \text{ cm}^{-1}$  are present. In general, the intensities of these peaks increase with increasing concentration of DMEDES, which suggests an increasing concentration of  $\text{CH}_3$  groups on the surface. The composition with 74% PhTES-26% DMEDES does not follow this trend precisely, showing slightly less intensity for  $\text{CH}_3$  than the sample with 66% PhTES-34% DMEDES.

Previously, it was found that melting gels are hydrophobic. Both melting gels with only phenyl substitutions<sup>1</sup> and melting gels with only methyl substitutions<sup>2</sup> show this behavior. The results of the measurement of the contact angle show that all compositions have a contact angle greater than  $90^\circ$ , with the highest value, where  $\theta = 102^\circ$  for the sample with composition 66% PhTES-34% DMEDES.

## V. Discussion

Gels formed with PhTES-DMEDES behave as melting gels, which are rigid at room temperature, soften around  $100^\circ\text{C}$  and can be transformed into hybrid glasses at their temperature of consolidation. PhTES has three ethoxy groups which hydrolyze allowing the formation of an inorganic network, whereas DMEDES has only two ethoxy groups, which means that the number of hydrolyzable groups is reduced. The temperature of consolidation of the melting gels varies with the composition as listed in Table I. The temperature of consolidation increases with increasing DMEDES. The increase in DMEDES means an increase in the number of  $\text{CH}_3$  groups, which in turn means the  $\text{Si-O-Si}$  backbone contains fewer

cross-links. In fact, by hydrolysis and polycondensation of DMDES alone, PDMS is formed, consisting entirely of linear molecular chains.<sup>8,9</sup> The dangling  $\text{CH}_3$  groups make it difficult to pack chains together, even with the weak interactions between chains.

According to thermogravimetric analysis, in the first step of decomposition the recorded weight loss increases in samples with more DMDES. This reflects the polycondensation reaction between the terminal groups  $-\text{OH}$  and/or  $-\text{OC}_2\text{H}_5$ , which creates  $\text{Si}-\text{O}-\text{Si}$  bonds and releases water or ethanol. The main exotherm in Fig. 1 is located around  $600^\circ\text{C}$ . This exotherm is slightly lower than the one found in the pure phenyl system with PhTES and DPhDES, which was around  $610^\circ\text{C}$ ,<sup>1</sup> but significantly higher than the one found in the pure methyl system with MTES and DMDES, which was around  $440^\circ\text{C}$ .<sup>25</sup>

The increase in the temperature of consolidation with increasing concentration of DMDES may mean that the PDMS chains are longer, requiring more cross-links to form before reaching consolidation. Alternatively, increasing the DMDES content in the gel, which makes the network more flexible, leads to a smaller number of terminal  $\text{Si}-\text{OH}/\text{Si}-\text{OC}_2\text{H}_5$  groups, requiring a higher temperature for the condensation-polymerization. The thermal behavior determined using differential thermal analysis and differential scanning calorimetry support the observation that more methyl groups delay the polymerization and consolidation of melting gels to higher temperatures.

The glass-transition temperatures with PhTES-DMDES are between the values observed for the methyl only system,<sup>25</sup> where all  $T_g$  values are lower than  $0^\circ\text{C}$ , and those values for the phenyl only system, where  $T_g$  values are greater than  $0^\circ\text{C}$ .<sup>1</sup> The trend in general is that the glass-transition temperature increases with an increase in the concentration of DMDES, except the sample with 74% PhTES-26% DMDES which is  $4^\circ\text{C}$  higher than 80% PhTES-20% DMDES.

The glass-transition temperature  $T_g$  observed in scanning calorimetry is often associated with polymer chain stiffness, in this case, the siloxane chains formed during the sol-gel process. A decrease in the  $T_g$  occurs with an increase in the number of methyl and phenyl organic groups, meaning a decrease in the number of oxygen bridges between siloxane chains.<sup>39</sup> Moreover, higher numbers of non-hydrolytic organic groups lead to the formation of more linear polysiloxanes as are present in PDMS. An increase in the percent of the di-substituted siloxane limits the cross-linking of the molecular chains into three-dimensional networks. A low glass-transition temperature in melting gels indicates a higher concentration of linear polymeric chains. The  $T_g$  of PDMS, which is formed only from the linear polysiloxane chains is  $\sim 100^\circ\text{C}$ .<sup>40</sup>

The isothermal experiment illustrated in Fig. 3 shows that the  $T_g$  increases following the isothermal treatment. The increase in the glass-transition temperature during the isothermal treatment appears to be related to cross-linking, similar to the phenomena that occur during consolidation. As mentioned before,  $T_g$  is taken to be an indication of the number of oxygen bridges in the organic polysiloxanes.<sup>25</sup> The increasing number of oxygen bridges leads to the organic modified polysiloxanes becoming less flexible and to an increase in their  $T_g$  toward higher temperatures. The increase in the  $T_g$  values after the isothermal treatment indicates that during the consolidation the  $-\text{OH}$  and/or  $-\text{OC}_2\text{H}_5$  groups bonded to the  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  chains are brought into proximity in such a way that cross-linking can take place. As a consequence of the increased degree of cross-linking, the organically modified polysiloxanes chains become stiff, locked in a three-dimensional network that no longer softens. Some of the  $-\text{OC}_2\text{H}_5$  groups are eliminated during the isothermal treatment as further condensation reactions occur. This is supported by a decrease in the exotherm after the isothermal experiment, compared to the exotherm in the

original constant heating treatment. As with all melting gels, the consolidation temperature is associated with the completion of the cross-linking of the polysiloxanes, which is irreversible. Once the consolidation is carried out, the hybrid glasses no longer soften.

The FT-IR and Raman spectra show that  $\text{Si}-\text{C}$  bonds remain intact during the hydrolysis-polycondensation reactions and gelation. The  $\text{Si}-\text{CH}_3$  and  $\text{Si}-\text{C}_6\text{H}_5$  bonds are retained as a part of the polymer network in the consolidated hybrid glasses. The Raman spectra of the hybrid glasses are presented in Fig. 5(a), where the peaks due to the presence of the organic groups are more intense than those assigned to the  $\text{Si}-\text{O}-\text{Si}$  backbone. The same phenomena where the vibrations of the organic groups have higher intensity than the silica network was observed for the hybrid glasses obtained in the MTES-DMDES system<sup>2</sup> where only  $\text{Si}-\text{CH}_3$  bonds were present, and the PhTES-DPhDES system<sup>1</sup> where only  $\text{Si}-\text{C}_6\text{H}_5$  bonds were present.

In this study, the peaks for phenyl groups are more intense than the peaks for methyl groups. As described in the experimental section, the Raman spectra were recorded under the optical microscope. The penetration of the excitation laser beam for this setup is  $\sim 0.5\ \mu\text{m}$ . The higher intensity of the vibration attributed to organic groups can be explained by the large quantity of these groups on the surface. Moreover, the higher intensity of the peaks characteristic of  $-\text{C}_6\text{H}_5$  compared with those assigned to  $-\text{CH}_3$  can be explained by the higher volume occupied by the phenyl groups and also by the steric hindrance between these groups. This leads to the likelihood that the phenyl groups are on the surface of the hybrid glasses. The presence of organic groups on the surface of melting gels contributes to melting gels having contact angle values that are greater than  $90^\circ$ , with respect to water. All the melting gels with mixed aliphatic and aromatic groups were hydrophobic.

The sample with 80% PhTES-20% DMDES has behavior and properties influenced by the PhTES, which makes it more like samples in the PhTES-DPhDES system, whereas the samples with 66% PhTES-34% DMDES, 57% PhTES-43% DMDES, and 50% PhTES-50% DMDES have behavior influenced by the DMDES and their properties are closer to those in the MTES-DMDES system. For the sample with 74% PhTES-26% DMDES, the behavior is transitional between these systems. This ratio gives a balance of the properties of all aliphatic and all aromatic.

In the all aliphatic substitutions, there are no double bonds. The bonding between chains that have methyl groups is weak, because there is little polarization of electrons on the methyl group, and little dipole-dipole interaction between siloxane chains. In the all aromatic substitutions, there are double bonds. These make the phenyl groups more polarizable, which, along with the larger size of the group, create attraction between phenyl groups and other nuclei. It is hard to know exactly which effects are controlling the cross-linking in the melting gels with mixed substitutions. On the one hand, more polarizable groups should bring chains together, allowing for cross-linking and bringing the consolidation temperature down. This trend is observed, with the composition with the most phenyl groups having the lowest consolidation temperature. On the other hand, the phenyl groups disrupt the symmetry of the siloxane chains, and this contributes to increasing the glass-transition temperature. In the one composition that does not follow the trend, 74% PhTES-26% DMDES, where the glass transition is slightly higher than for the sample with 80% PhTES-20% DMDES, it may be a combination of the two effects. To further understand the effects of polarizability and symmetry, other substituted alkoxysilanes can be mixed together. Especially for imprint lithography, where the temperature of the glass transition is critical to maintaining good definition when a pattern is being transferred to a surface, it is important to be able to adjust the glass transition through the choice of substitutions.

## VI. Conclusions

In summary, the temperatures for softening and consolidation can be changed in melting gels by changing the ratio of mono-substituted to di-substituted siloxanes. In addition the range between softening and consolidation can be adjusted by changing the substituted group, for example, from phenyl to methyl, or more generally from aromatic to aliphatic. These substitutions, in turn, determine the glass-transition temperature, the consolidation temperature, and the difference in temperature between the two, for a given composition.

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