2. Experimental

2.1. Chemicals

All the chemicals for the vinyl-terminated system were purchased form Gelest Inc. Two different molecular weight pre-polymers were used to form the networks. For the vinyl system, the low molecular weight oligomeric material used was 1, 3- divinyl tetramethyl-disiloxane of molecular weight 186.4 g/mol. The high molecular weight pre-polymer used was vinyl-terminated polydimethylsiloxane (PDMS) (22,000 g/mol). The crosslinker was tetrakis(dimethylsiloxy)silane and a platinum-divinyl tetramethyl disiloxane complex in xylene, also known as Karstedt's catalyst [1], was used to catalyze the end-linking reaction. Molecular weights of the PDMS pre-polymers as used from Gelest Inc. could have a distribution. We did not perform investigations on the molecular weight distributions due to constraints.

In the Silanol terminated system, the pre-polymers used were silanolterminated PDMS of molecular weights 750 g/mol and 18,000g/mol obtained from Gelest. Tetraethylorthosilicate (TEOS) of 98% purity from Aldrich was used as the crosslinker. Dibutyl tin dilaurate, 25% in cyclic dimethyl siloxane from United Chemicals Technologies Inc. was used as the catalyst. The hydrolysis/condensation reaction results in the formation of 4 ethanol molecules per TEOS in the hydrolysis reaction, consuming 4 water molecules followed by the release of 4 water molecules per molecule of TEOS on condensation. The total hydrolysis/condensation reaction consumes 4 moles of water and produces 4 moles of ethanol and water per mole of TEOS. Ethanol is generally outgased and or extracted from the final network. For our in situ studies, forced outgassing using a vacuum was not possible leading to an even slower rate of gelation and network formation. The rate of increase in molecular weight was lower in the hydroxyl system as compared to the vinyl system as evident from a much longer gelation time. For chemically driven phase-separation the extent of reaction parallels the thermal quench depth in traditional thermally controlled phase-separation. In this context, the hydrosilation system represents a deep quench condition, far from the critical point, while the hydrolysis/condensation system represents a shallow quench condition near the phase separation boundary for much of the network forming reactions.

2.2. Network Formation

Vinyl-terminated, bimodal networks were formed using 98 to 99.5 mole percent of short chains and the remainder long chains. This represents roughly a 50% mixture by volume. A stoichiometric amount of crosslinker was employed in all the formulations. Catalyst loading appears to be vital to production of the spinodal-like structure in the vinyl system, presumably due to the influence of the rate of crosslinking on the development of the spinodal-like morphology. It was found that the minimum amount of catalyst for gelation and network formation was optimal and in order to achieve relatively low catalyst concentrations the initial catalyst solution was diluted in toluene to 10 % by volume of the initial solution. Through trial and error it was found that 0.5 mg of this diluted catalyst per gram of base polymer mixture was optimal for production of the spinodal-like structure. Networks produced under these conditions showed phase separation in bulk when synthesized in a glass vial as well as when synthesized between glass cover-slips. It should be noted that thin films prepared by placing a drop of the reaction mixture on a single glass cover slip, open to the atmosphere, did not display phase separation. This may be associated with the sensitivity of the hydrosilation reaction to atmospheric oxygen.

The hydrolysis/condensation system consisted of 98.5 mole percent short chains (about 50% by mass) and also utilized a stoichiometric amount of tetraethylorthosilicate, TEOS, crosslinker. Dibutyl tin dilaurate catalyst loading was varied from 2-5% by weight of the polymer mixture. It was observed that higher catalyst loading (5%) was needed to synthesize networks that displayed phase-separation. Using 0.2% catalyst loading [2] as indicated in literature did not work for our system as at such low catalyst concentrations we were unable to obtain gelation in the samples.

2.3. Light Scattering Measurements

Light scattering was performed on samples prepared between glass cover slips that were 1 mm in thickness. A 20 mW Helium-neon gas laser at 632.8 nm wavelength was used. Using a single pinhole near the sample, the scattering pattern was projected on a screen and imaged with a CCD camera, Princeton instruments Optical Multichannel Analysizer (OMA) camera [3, 4]. Background scattering from an identical sample except for the absence of crosslinker was subtracted from the light-scattering patterns. The data was corrected for $1/r^2$ decay due to the flat projection of the scattering pattern; and the 2D data was radially averaged. A schematic of the light scattering setup is shown in the figure below.

3.2.1. Hydroxyl Terminated System

Samples were prepared on microscope cover slips, both open to atmosphere and sandwiched, as described above. The reaction in the hydroxyl-terminated system was much slower as compared to the vinyl-terminated system (Fig. 15). Usually, these samples took over 4-5 hours to gel. The samples were exposed to ambient H_2O (air humidity). Initially, a ring pattern observed in the hydroxyl-terminated system was believed to be due to spinodal decomposition. But after inspection of the optical micrographs (Fig. 22) it was found that low dispersion spherical domains formed, resulting in the ring pattern. The light scattering pattern in Fig. 22 (inset) displayed multiple concentric rings similar to the sphere function given by eq. 48 [23].

$$I(q) = \rho_0^2 v^2 \frac{9(\sin qR - qR \cos qR)^2}{(qR)^6}$$
(48)

where R is the sphere radius, q is previously defined, ρ^2 is the contrast (Δn^2 for light scattering), and v is the volume of the spheres, assuming small difference in the refractive indices. The optical micrograph in Fig. 22 shows the morphology of the phases formed which are reminiscent of nucleation and growth. Fig. 23 is a log-log plot of scattered intensity versus wave-vector q for a sample with morphology as shown in Fig. 22. The data of Fig. 23 was fit using the maximum entropy method [24-32] that has been demonstrated to yield a good approximation of the particle size distribution for spherical particles [23, 26, 27]. The code for the program is available on the web [25].



Figure 22. Nucleation and growth mechanism of phase separation observed in the hydroxyl-terminated system, inset shows the concentric ring pattern observed in light scattering from the specimen.

The maximum entropy method is widely accepted as a reasonable approach to obtaining the most-likely distribution function and it has been demonstrated to be effective at recreating a wide range of particle-size distributions from model systems. By fitting the scattered intensity using the maximum entropy method, the line in Fig. 11, the size distribution of the spherical domains was obtained as shown in Fig. 24. Fig. 24 shows that the spherical domains display a bimodal distribution, consistent with the micrograph in Fig. 22. The distribution for the two modes are extremely narrow, $\sigma \sim 2 \mu m$ indicating a fairly narrow time-span for nucleation. The narrowly distributed domains are consistent with Fig. 15. A probable mechanism for this to occur could be as follows; initially the condensation reaction proceeds at a rapid rate to a low conversion. This could lead to the nucleation on the heterogeneous nucleation sites in the system. The micrograph in Fig. 22 and its volume distribution obtained in Fig. 24 support this, i. e. large domains made of $9 \pm 1 \mu m$.



Figure 23. Light scattering plot of log-scattered intensity versus log-q; line indicates a fit to the data using the maximum entropy method of Jemain and Ilavsky [21] for polydisperse spheres.

The nucleation depletion is associated with the reduction in conversion rate, (see Fig. 15.). The nucleation depletion, formation of domains and the absence of remaining unused heterogeneous nuclei could lead to the observed large scale size with narrow size dispersion. Later, when crosslinking has prevented the coalescence of these domains, the slow production of highly branched species in the predominantly long-chain phase could lead to a second nucleation event in the gel network, with nucleation on regions of high crosslink density formed in the reaction. These late stage domains might be expected to be smaller since they nucleate later and since their growth occurs in a gel network. A broader distribution is also expected, $4 \pm 2 \mu m$ as observed in Fig. 24. This discussion must remain speculative since the details of composition variations in such a reaction system are difficult to observe.



Figure 24. Particle volume distribution function f(D), plotted against particle size.

3.2.2 Gelation in Hydroxyl-terminated PDMS

According to Carothers equation [8], for gelation to occur, the critical extent of reaction, p_c , has to be attained. For the hydroxyl terminated system, crosslinking occurs by the reaction of 4 moles of the di-functional precursor PDMS and one mole of the tetra-functional crosslinking agent. The average functionality of the system can then be given by,

$$f_{avg} = \frac{(1 \times 4) + (4 \times 2)}{1 + 4} = 2.4$$

From which we can calculate the critical extent of reaction as,

$$p_c = \frac{2}{f_{avg}} = 0.83$$

So as will be discussed later the hydroxyl-terminated system can undergo gelation even with around 15-20% solubles.