Critical extent of reaction of a polydimethylsiloxane polymer network

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A direct rheological technique was used to measure the critical time for gelation, t_c, of a well characterized polydimethylsiloxane (PDMS) polymer network. This technique is based on the observation that the gel point of crosslinking systems occurs at the instant at which the viscoelastic behaviour reduces to power-law relaxation (critical state described by the gel equation). The extent of reaction, $p(t)$, was measured by a Fourier-transform infra-red method. The measured value of the critical extent of reaction, $p_c = p(t_c) = 0.57 \pm 0.01$, agrees extremely well with the value predicted by mean-field theory. This agreement is an independent confirmation of the observation that power-law relaxation is a property of the polymer at the gel point.

INTRODUCTION

The study of the critical behaviour of crosslinking polymers has always been hampered by the lack of a direct method for determining the gel point. The experiments had to depend on extrapolation. This has changed recently, when advances in the understanding of gelation made it possible to measure the instant of chemical gelation, the gel point, directly and accurately[1]. Then, the measured critical conversion at the gel point, p_c, can be compared with the predictions of gelation theory.

Several studies have compared the theoretically predicted gel point with experiments. Valles et al.[2] and Gottlieb et al.[3] report a good agreement between predicted and observed gel points in chemically crosslinked siloxane networks. Macosko and Saam[4] in a similar study used chemically crosslinking polyisobutene and report a substantial side-reaction that consumes silanes when experiments are conducted at high temperatures. Bidstrup and Macosko[5] report a good agreement with branching theory in the case of epoxy–amine crosslinking, and Adam et al.[6] studied several polycondensation reactions. In all these cases, the gel point was obtained either by extrapolation of viscosity data or by dissolution experiments. However, a recently developed technique provides the means for direct determination of the gel point by rheological measurements[1,7]. This method is based on the observation that the instant of gelation is characterized by power-law relaxation behaviour. The linear viscoelastic material functions at this point could be described fully by the gel equation[8,9]:

$$\tau(t) = \int_{-\infty}^{t} (t-t')^{-n} \dot{\gamma}(t') \, dt'$$

This paper utilizes the novel rheological method to determine the critical extent of reaction, p_c. We adopt the following strategy to achieve this goal. We take a well defined polymer system, accurately determine molecular weight and functionalities of the components by suitable methods, and allow the reaction to proceed under carefully controlled conditions. The extent of reaction, $p(t)$, is followed using Fourier-transform infra-red ($FTi.r.$) spectroscopy. The gel point, t_c, is determined by dynamic mechanical measurements in a parallel experiment. The critical extent of reaction at the gel point, $p_c = p(t_c)$, is determined by combining the information obtained from the two experiments. This experimentally determined value can then be compared with the critical extent of reaction for gelation as predicted by branching theory.

EXPERIMENTAL

Materials

The polymer used in this study is a linear, vinyl-terminated polydimethylsiloxane (PDMS), which is crosslinked with a four-functional siloxane, tetrakis (dimethylsiloxy)silane, both purchased from Petrarch Systems Inc. The hydrosilation reaction is catalysed by cis-dichlorobis(diethylsulphide) platinum(II) catalyst. This system was suggested by the work of Valles and Macosko[10]. The raw PDMS was first filtered and heated at 140°C under high vacuum for 12 h to remove about 1.4 wt% of low-molecular-weight species and other impurities. The crosslinker was distilled with a Perkin–Elmer spinning band column prior to use and had a purity higher than 99.99% as determined by gas–liquid chromatography (g.l.c.).

Physical characterization of PDMS

The intrinsic viscosity of the purified PDMS in toluene was measured using a Cannon–Fenske routine viscometer no. 25. The concentration of the solutions varied from

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1.08 to 3.07 g PDMS/dl solution. All the measurements were made at 25°C. The intrinsic viscosity $[\eta]$ was measured as $13.16 \, \mathrm{ml \, g^{-1}}$. A measure of the number-average molecular weight, $\bar{M}_n$, is given by calibration relations for PDMS in toluene at 25°C[11]:

$$\bar{M}_n = 513.9(P)^{-0.8618}[\eta]^{1.3822} \qquad 5 < [\eta] < 20 \, \mathrm{ml \, g^{-1}}$$

$$\bar{M}_n = 353.1(P)^{-0.829}[\eta]^{1.5195} \qquad 12 < [\eta] < 85 \, \mathrm{ml \, g^{-1}}$$

where $P = \bar{M}_w/\bar{M}_n$ is the polydispersity. These relations have been derived from published data[12-14] and corrected for polydispersity $P > 1$. Gel permeation chromatography (g.p.c.) was performed using the purified PDMS on a Waters g.p.c. instrument with toluene as solvent. The instrument calibration was calculated from polystyrene standards and applied to PDMS using the universal calibration scheme with Mark–Houwink constants obtained from Lapp *et al.*[13]. Vapour-pressure osmometry (v.p.o.) with toluene as solvent was performed on a Corona Wescan Molecular Weight Apparatus model 232A. ^{1}H n.m.r. measurements were performed on the purified PDMS at the Ben-Gurion University, Israel.

Analysis of molecular-weight data

The results of the molecular-weight measurements are shown in *Table 1*. Different methods of measuring the molecular weight seem to be sensitive to different molecular characteristics and yield different values. Lapp *et al.*[13] report a lack of sensitivity in their calibration curves to low-molecular-weight species. The intrinsic viscosity is sensitive to low-molecular-weight fractions and to molecular configuration. That is, a linear chain will not have the same effect on viscosity as a cyclic of the same size. This could explain why the molecular weights obtained from intrinsic viscosity are much lower than those obtained from g.p.c. and n.m.r., as the vacuum stripping is not totally effective. Also, the $\bar{M}_n$ value obtained from intrinsic viscosity depends strongly on the polydispersity $P \simeq 2.9$, which is taken from the g.p.c. measurement.

For our purposes, the most useful measure is the number of vinyl groups, or the apparent molecular weight determined by vinyl-sensitive analysis. N.m.r. measures the concentration of vinyl groups. Assuming an average functionality of 2, the agreement between the n.m.r. and g.p.c. measurements is very good, giving confidence in the values. Therefore, a value of $\bar{M}_n \simeq 10\,000$ is used in the calculations.

Stoichiometry

The stoichiometric ratio, r, of the PDMS system is defined as the initial ratio of silane to vinyl groups. This can be calculated once the molecular weights of the reactants and their functionality are known. The functionality of the crosslinker was measured by ^{29}Si n.m.r. on a neat sample to be 3.97, which shows no
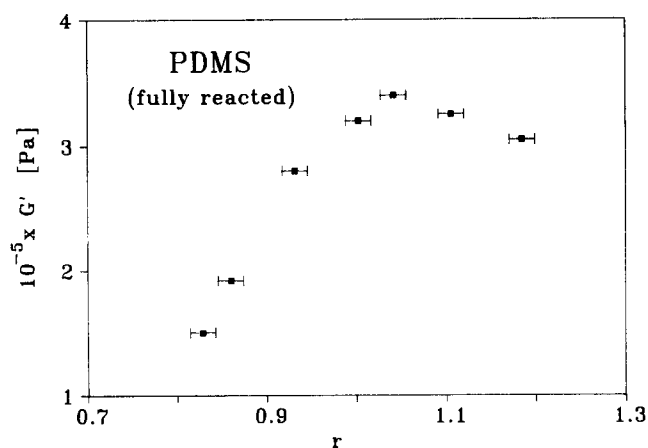
Table 1 Molecular weight of linear PDMS

Method	$\bar{M}_n$	$\bar{M}_w$
Intrinsic viscosity	7500	21800
Gel permeation chromatography (g.p.c.)	10000	29000
Vapour-pressure osmometry (v.p.o.)	7900	–
Nuclear magnetic resonance (n.m.r.)	10500	–

Figure 1 Storage modulus, G', of fully cured PDMS samples as a function of the stoichiometric ratio, r, at $T = 34°C$ and $\omega_0 = 0.5 \, \mathrm{rad \, s^{-1}}$

significant deviation from the ideal value of 4. The functionality of the prepolymer is assumed to be equal to 2. Alternatively, the stoichiometric ratio can be calculated directly from the concentration of reactive end-groups present in the components. Details of the sample preparation are reported by Chambon[15].

Stoichiometry and side-reactions

A major problem in the study of most model networks arises from side-reactions[4,16]. As much as 30% of the silane was shown to be consumed by various redistribution reactions, when the crosslinking was carried out at moderately high temperature of 65–110°C. However, our particular polymer system was shown to crosslink without any significant side-reaction, as long as the crosslinking reaction occurred at low temperatures[16], such as 34°C, used for this study. In the absence of significant side-reactions, balanced stoichiometry should lead to the final network with the highest elasticity. This was estimated by measuring the dynamic storage modulus, G', of fully cured samples of different composition, at low frequency, $\omega_0 = 0.5 \, \mathrm{rad \, s^{-1}}$, and small shear strain amplitude, $\gamma = 0.01$ (*Figure 1*). At this low frequency, the value of the modulus measured is close to the equilibrium modulus of the network, and is directly representative of its elasticity. The samples of Chambon and Winter[8,9] were found to have a stoichiometric ratio of about $r = 1.04$, provided the value of $\bar{M}_n \simeq 10\,000$ was used in the stoichiometry calculations (see *Figure 1*). If the other (lower) $\bar{M}_n$ values as measured by v.p.o. and intrinsic viscosity are used in the calculations, the most elastically effective network would occur at $r < 1$, which is not likely. Also, computer simulations of end-linked tetrafunctional systems by Leung and Eichinger[17] indicate that the most effective elastic networks are produced by stoichiometric systems. Furthermore, crosslinker-deficient mixtures produce less effective elastic networks than those using excess crosslinker, supporting the trend seen in *Figure 1*. Therefore, the g.p.c. and n.m.r. measurements are taken to be an accurate measure of the molecular weight.

FTi.r. measurements

The reacting mixture was prepared as described before and split into two samples, one for the rheometer and the other for the *FT*i.r. Both experiments were conducted at the same temperature, 34°C, and data were taken at

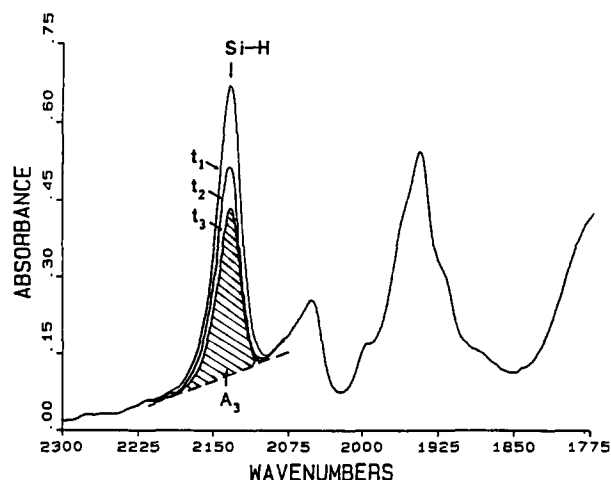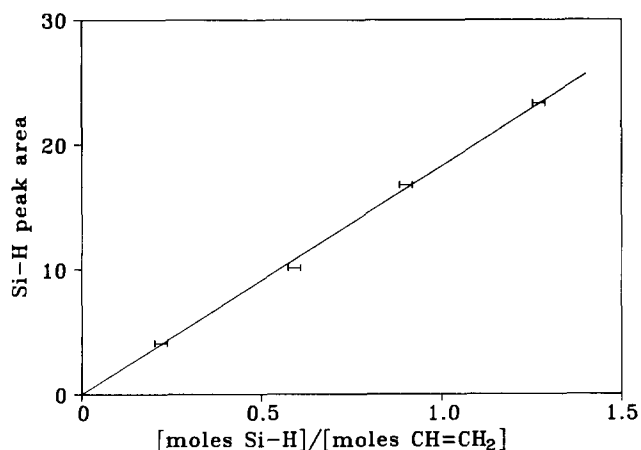**Figure 2** *F*Ti.r. absorbance spectra of the curing PDMS at different times, t_i, and at $T=34°C$

Figure 3 SiH absorption as a function of the ratio SiH/CHCH$_2$ at $T=34°C$

the same time interval of 1.05 min. To ensure direct correlation between the two experiments, the thermocouples in the two instruments were calibrated just before the experiment, and adjusted to ±0.5 K agreement.

An infra-red absorption technique was used to monitor the curing kinetics of the PDMS nework with balanced stoichiometry. The measured decrease in the total integrated intensity of the silane (Si–H) stretching band at 2134 cm^{-1} (*Figure 2*) gave the extent of reaction as a function of curing time, as was done in a previous study[10]. Without any side-reactions, the changes in Si–H concentration were taken to be due only to the reaction between silane and vinyl groups. Concentrations of silane end-groups were determined by comparison with a previously determined calibration curve (*Figure 3*). The calibration curve was constructed using the measured intensities of the silane stretching vibration for four different samples of known silane concentration. These were prepared by mixing known quantities of the PDMS prepolymer and the silane crosslinker, without any catalyst. As is evidenced by the linear dependence of absorption on silane concentration, Beer's law[18] was valid for the range of stoichiometric ratios of interest. That is, within this range, the Si–H concentration is directly proportional to the area of the peak.

To follow the kinetics, a frozen, unreacted sample was thawed and injected into a preheated Harrick variable-temperature cell. The temperature of the cell was maintained at a constant temperature of 34±0.5°C. A 0.25 mm spacer maintained the thickness of the sample in the cell. The IBM/98 Fourier-transform infra-red (*F*Ti.r.) spectrometer automatically recorded spectra of the reacting sample every 1.05 min at 2 cm^{-1} resolution. Some 48 scans were signal-averaged for each file (data point). The time of the 24th scan was taken to be the time corresponding to the file as a whole.

For each data point, the following equation determined the extent of reaction, p_{Si-H}, at a time t_i of the curing process:

$$p_{Si-H}(t_i)=[A_0-A(t_i)]/A_0$$

where A_0 is the Si–H peak area of the initially unreacted sample and $A(t_i)$ is the peak area at subsequent times of the reaction (*Figure 2*). The integrated intensity under the broad peak at 1943 cm^{-1} was observed to remain nearly constant during the course of the reaction, and its average value was used as an internal standard of calibration for the silane peak. The Si–H peak areas recorded each minute were reduced to this standard value.

The recorded kinetics of the reacting PDMS network are shown in *Figure 4*. The area $A(t_i)$ for each data point changes by approximately 0.5% from one measurement to another, which is close to the accuracy of the *F*Ti.r. measurement for the range of conversion considered. The short intervals in *Figure 4* without data points were caused by data storage problems, but are far outside the range of interest for this paper. The relative change of properties during an experimental measure can be estimated by means of a dimensionless quantity known as the mutation number[7]. In this case, this is defined as:

$$N_{mu}=t_{exp}\frac{1}{p}\frac{\partial p}{\partial t}$$

The mutation number of our experiments was estimated to be less than 0.01. As a result, the change of the Si–H peak area during the recording of the 48 spectra was sufficiently small (<1%) to ensure very precise determinations of conversion as a function of reaction time.
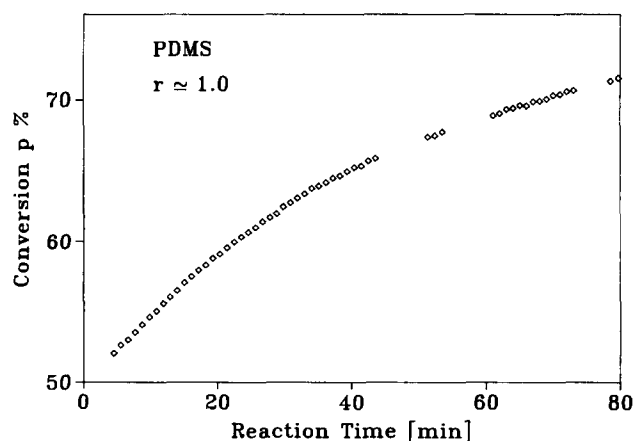

Figure 4 Degree of conversion, p, as a function of curing time for PDMS with balanced stoichiometry; p is measured by SiH absorption intensity

MEASUREMENT OF CRITICAL EXTENT OF REACTION

The instant of gelation occurs at the crossover point of the loss and storage moduli as long as the system is stoichiometrically balanced[8,19]. Therefore, the critical reaction time for gelation, t_c, can be determined directly by dynamic mechanical measurements in the rheometer (*Figure 5*). The extent of reaction as a function of time, $p(t)$, is measured by FTi.r., as described in the previous section. From the critical reaction time for gelation, t_c, and the extent of reaction as a function of time, the critical extent of reaction for gelation, p_c, has been determined experimentally to be 0.57 ± 0.01.

The measured p_c is influenced by the error in the conversion measurements and the effect of side-reactions, both of which have been shown to be negligible. There is, however, some uncertainty in obtaining t_c due to the slight differences between the reaction in the FTi.r. and in the rheometer, even though the two experiments were performed simultaneously, under practically identical conditions, and on samples with identical chemical composition.

COMPARISON WITH THEORY

There are two significantly different approaches to the theory of structure evolution in curing systems. The first is a mean-field theory developed by Flory[20] and Stockmayer[21], commonly referred to as the classical theory; the second is based on percolation[22]. The classical theories are widely accepted to predict the gel point quite accurately. But their predictions of structure evolution are not considered to be very realistic in the region close to the gel point. In a recent paper, Martin et al.[23] say that neither theory is capable of adequately describing the gelation process in the vicinity of the gel point in the case of a sol–gel system. In this paper, we are concerned only with the prediction of the gel point. For this purpose, a more general form of the Flory–Stockmayer theory, the recursive method of Macosko and Miller[24] based on a combinatorial approach, is used. The critical extent of reaction for gelation, p_c, is given by the relation:
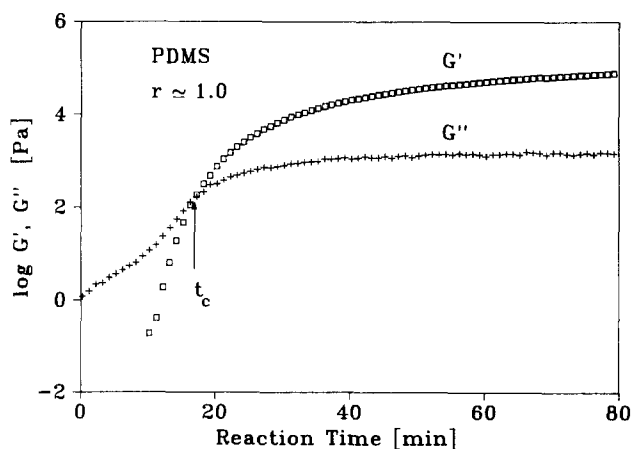
$$rp_c^2 = \frac{1}{(f-1)(g-1)}$$

Figure 5 Curing curve of PDMS with balanced stoichiometry, at $T=34°C$ and $\omega_0 = 0.5 \, \text{rad s}^{-1}$. The critical reaction time for gelation is the time at which the G' and G'' curves cross

where r = stoichiometric ratio, f = functionality of the prepolymer and g = functionality of the crosslinker.

An interesting prediction is that p_c is independent of the polydispersity of the prepolymer used, though it affects other molecular parameters[25]. The predicted value of the critical extent of reaction obviously relies on an accurate knowledge of the parameters r, f and g. Of these, the most difficult value to obtain is that of the stoichiometric ratio, r, which has been found to be $r = 1.04 \pm 0.05$, based on molecular-weight measurements, which have a precision of about $\pm 5\%$. The well defined functionalities of the two components in this case preclude them as a source of any significant error in the predicted value of p_c. In our case, $r = 1.04 \pm 0.05$, $f = 2$ and $g = 3.97$ yield a value for the critical extent of reaction $p_c = 0.57 \pm 0.014$. (It should be mentioned that uncertainty in the molecular weight of the PDMS prepolymer led Chambon and Winter[9] to an inaccurate value of $r = 1.32$ for the most elastically effective network, which normally occurs at or near balanced stoichiometry.)

It should be emphasized that measurement of the extent of reaction by spectroscopic methods and comparison with the prediction of gelation theory is an indirect method to determine the sol–gel transition point, and of limited significance. There are numerous experimental difficulties in using the predictions of gelation theory to determine the gel point. Rheology presents a much more powerful and precise technique to achieve this objective. This can be evidenced by the dramatic change in properties of the reacting mixture as it passes through the gel point (see figure 3 of Winter and Chambon[8]). This shows the frequency dependence of the dynamic moduli of PDMS with balanced stoichiometry at intermediate stages of conversion. The change in the extent of reaction between the times $(t_c - 2)$ and $(t_c + 2)$ min is only about 1.5%. On the other hand, the change in the rheological behaviour has been dramatic, as the crosslinking polymer moves from liquid-like behaviour to the critical gel state, and then to solid-like behaviour. The true power of the rheological technique can be realized when the stoichiometric ratio is imbalanced. The dynamic moduli still exhibit a power-law dependence on the frequency of deformation, as shown by Chambon and Winter[9]. Holly et al.[1] utilized this property to develop a new technique to determine the instant of gelation in crosslinking polymers. Therefore, dynamic mechanical spectroscopy presents a powerful tool to determine the instant of sol–gel transition (gel point) of a crosslinking polymer network.

CONCLUSIONS

An excellent agreement has been obtained between the theoretical prediction and experimental observation of the critical extent of reaction at the gel point. The direct method of determining the instant of gelation, t_c, is very easy to use, and the extent of reaction can be monitored with FTi.r. Therefore, the critical extent of reaction, $p_c = p(t_c)$, can be determined with reasonable accuracy. On the other hand, it is still difficult to make predictions of the critical extent of reaction, p_c, even if the classical theory of Flory and Stockmayer gives a simple formula that predicts p_c. Difficulties arise from the insufficient knowledge of molecular parameters such as molecular-weight distributions and functionalities, which are

difficult to determine accurately. It is here that better methods have to be developed.

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