Kinetics of Polycondensation of Hydroxyfunctional Polydimethylsiloxane

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SYNOPSIS

The kinetics of polycondensation of hydroxyfunctional polydimethylsiloxane has been studied with a simple new inexpensive piece of equipment, i.e., the vibrating needle cure-meter. The order of reaction with respect to crosslinker and catalyst concentration has been determined to be unity and 0.24, respectively. The activation energy of the reaction has been found to be zero. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The curing of hydroxyfunctional polydimethylsi-loxane (HOPDMS) with trifunctional crosslinker such as vinyltrismethoxyethoxy silane in presence of the catalyst can be represented as
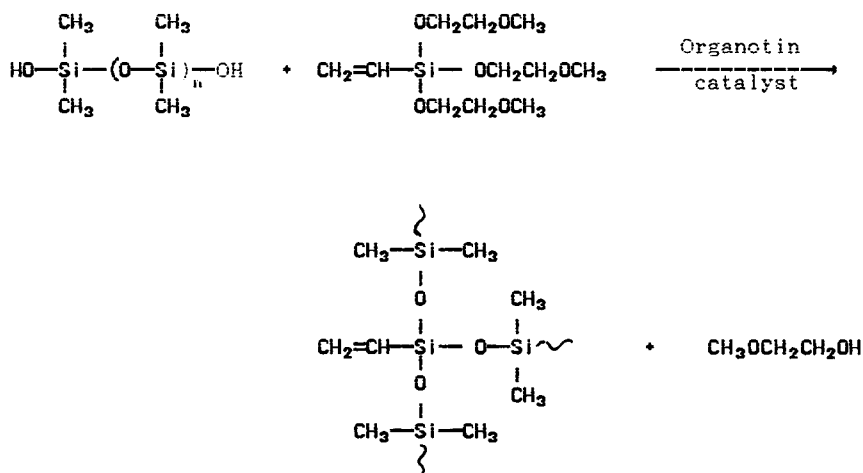
In the case of linear HOPDMS of molecular weight 67,000, the content of the OH groups is about 0.051% w/w. Unlike typical urethane chemistry, this relatively small number of hydroxyfunctional groups present on the chain makes it difficult to monitor the crosslinking reaction by chemical and spectroscopic methods. That is why crosslinking of these materials is monitored mostly through assessment of its viscosity up to the instant of gelation.[1-3]

In the present study, kinetics of the curing of HOPDMS has been carried out by means of a new simple and inexpensive instrument called vibrating needle curemeter (VNC) that can provide a good means of covering the whole range of the

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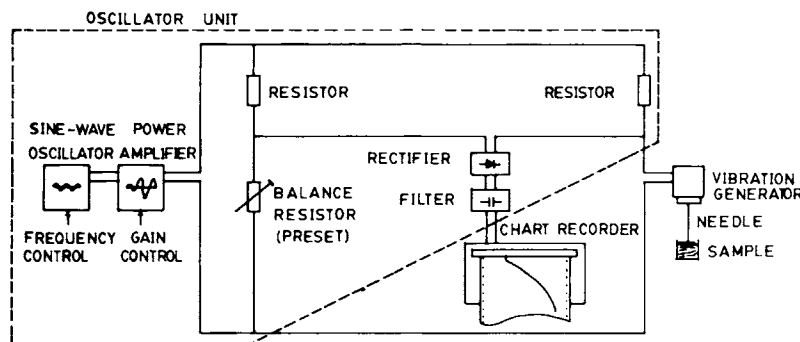* To whom correspondence should be addressed.

Figure 1 Simplified circuit diagram of the VNC.

rheological spectrum without interrupting the cure process.

EXPERIMENTAL

The liquid HOPDMS prepolymer used was Silopren C18 with quoted relative molar mass (M_n g/mol) 67,000 supplied by Bayer Ltd. The catalyst, dioctyltinmaleate (DOTM) (LT195, MW 459), was provided by Lankro Ltd. and the crosslinker vinyltris(methoxyethoxy)silane (VTMES) (A172, M.W. 280.4) by Union Carbide Ltd.

The material (mixture of HOPDMS, catalyst and crosslinker) was poured into a polyethylene cup, and the probe, vibrating at 40 Hz, was inserted to the standardized depth of 3 mm. The millivolt-time sweep for the curing of HOPDMS measures the complex modulus that is assumed to be function of the extent of reaction. The reaction was

Figure 2 Typical millivolt-time cure for curing of HOPDMS.

monitored over 30 min. The extent of the reaction (assumed to be proportional to the amount of OH groups reacted at time t) was measured at different time intervals, i.e., 5, 10, 15, 20, 25, and 30 min from the respective millivolt-time graph. For activation energy determination, the polycondensation reaction between stoichiometric amount of crosslinker and HOPDMS was carried out at different temperature, over the range of 10–90°C with an increment of 10°C.

Apparatus

The VNC has recently been developed at the Rubber and Plastic Research Association Technology Ltd. to monitor the increase in viscosity of polymer systems during polymerization.[4,5] It consists of a modified Ling Dynamic System TPO 25 oscillator unit and Ling Dynamic System 100 series vibrator connected to a chart recorder. The TPO 25 oscillator unit incorporates a Wien Bridge sine-wave oscillator having frequency control in the range of 1.5–25 kHz and a sine wave with amplitude between 0 and −2.2 V feeds a power amplifier.

The power-oscillator unit is modified so that the output of the power amplifier is fed to the vibrator via a bridge circuit. Any variation in the current drawn by the vibration generator will alter the balance of the bridge, and this can be measured by rectifying the out of balance waveform and displaying it on the chart recorder. A simplified circuit diagram is shown in Figure 1. A threaded socket attached to the vibrator is provided for fitting the needle to be used in measuring changes in rheology. The VNC can be operated at a lower frequency, i.e., 40 Hz, if the early stage of curing is of interest, where as for more sensitive changes in the later stages of cure, a higher frequency, e.g., 150 Hz, is required. A typical millivolt-time VNC curve for the curing of prepolymer is shown in Figure 2.
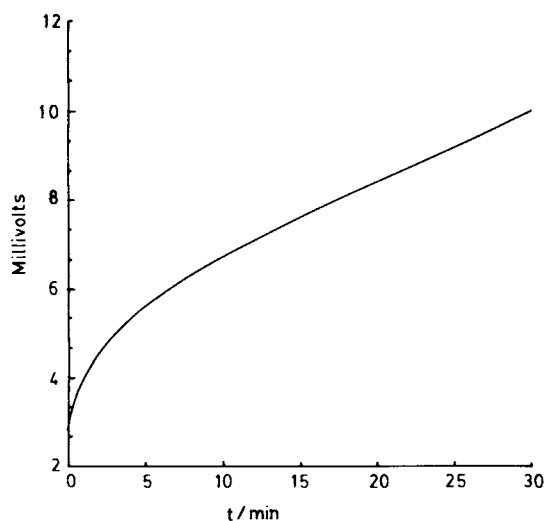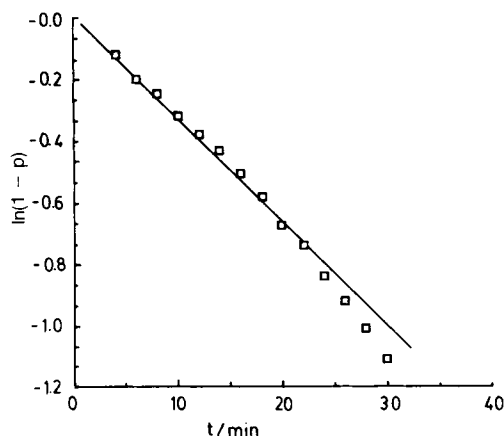
Figure 3 Variation of $\ln(1-p)$ with time for curing of prepolymer HOPDMS.

Rate of Reaction as a Function of Crosslinker and Catalyst Concentrations

A stock mixture containing 0.07% (w/w) catalyst (DOTM) in the prepolymer was made. To 15-g portions of this mixture, the crosslinker (VTMES) was added in portions 1 in the range of 0.008–0.8 g (0.05–5.0% w/w). The extent of the reaction was measured as stated before in the experimental procedure.

Less than stoichiometric[6] amount (0.7%), i.e., 0.44 g (0.27%), of crosslinker VTMES was added to 165 g of the prepolymer and mixed. Amounts of catalyst (DOTM) in the range of 0.0019–0.8 g (0.013–5.091%) were added to 15-g aliquots of the above mixture. The procedure was repeated as above.

RESULTS

Determination of Kinetic Constants

To study the kinetics of the crosslinking reaction it is useful to define extent of reaction p in terms of N_α, the total number of crosslinks which can be found at infinite time, and N_t, the number of crosslinks formed at any time t as

$$p = \frac{N_t}{N_\alpha} \tag{1}$$

The millivolt-time sweep for the curing of HOPDMS measures complex modulus and if it is assumed that this is a function of the extent p of reaction then

$$p = \frac{v_t}{v_\alpha} \tag{2}$$

where v_t is the output voltage in millivolts at time t and v_α is the output voltage in millivolts when the reaction is complete. The slow and long postgelation period of curing of HOPDMS made it difficult to obtain the value of V_α directly from the millivolt-time graph, so V_α was obtained by extrapolating the graph of output voltage over 30 min as function of the inverse time. The value of V_α was obtained by using the stoichiometric value of the crosslinker.

After defining the extent of reaction p, the first- and second-order rate equations can be expressed as follows:

$$\ln[1-p] = -k_1 t \tag{3}$$

$$\frac{1}{[1-p]} = k_2 t + 1 \tag{4}$$

The data for each composition of the series with crosslinker or catalyst variation when plotted according to the first-order rate equation followed a straight line for between 16 and 20 min with some small deviation after that time. A typical example is given in Figure 3. The data deviated markedly from linearity after about 12 min when plotted according to the second order equation (Fig. 4). Assuming that the linearity of this data indicates first-order kinetics, the slopes of the straight lines have been recorded in Table I as first-order rate constants. To confirm, the data were plotted according to the logarithmic form of the above equations that gave linear plot with slope of approximately unity only for the first order equation (Figs. 5 and 6).

$$\ln\{-\ln[1-p]\} = \ln k_1 + \ln t \tag{3a}$$

$$\ln\frac{1}{1-p} = \ln k_2 + \ln t \tag{4a}$$

Because k_1 depends on [OR]∘, [OH]∘, and [Sn]∘, it can be written that

$$k_1 = k[OH]^x_\circ[OR]^y_\circ[Sn]^z_\circ \tag{5}$$

where k is the proportionality constant. If [OR]∘ only is varied, then $k[OH]^x_\circ[Sn]^z_\circ$ will be a constant k' at a given temperature and

$$k_1 = k'[OR]^y_\circ \tag{5a}$$

By plotting $\ln k_1$ against $\ln[OR]∘$, order y with respect to [OR]∘ can be found. The same procedure can be used for the other reactants.
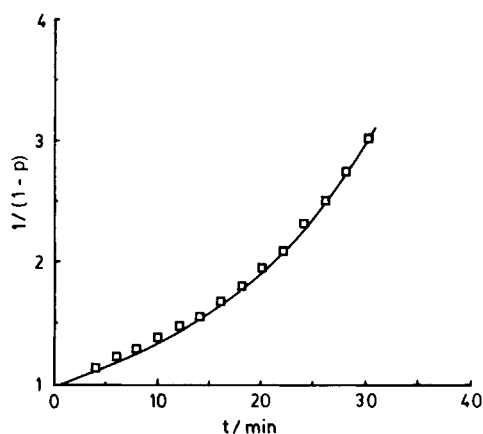
Figure 4 Variation of $1/(1 - p)$ with time for curing of prepolymer HOPDMS.

Figure 5 Plot of data for curing of HOPDMS according to first-order rate (log form) equation.

The different molecular weight of the same prepolymers when studied was found to contain the same concentration of OH groups (about one per 9000–12,000 MW) per unit chain length.[6] Because of this uncertainty in the number-averaged molecular weight of the prepolymer, the effect of variation of concentration of hydroxyl groups in the prepolymer on the rate of reaction was not studied.

Having confirmed that the reaction follows first-order rate equation, the data for the reaction carried out at different temperature (i.e., 10–90°C) were plotted according to eq. (3) and the rate constant (k) calculated. The log of k was plotted against the inverse of absolute temperature. The data gave a horizontal line with a zero slop, showing that the reaction has no activation energy over the range of 10–90°C.
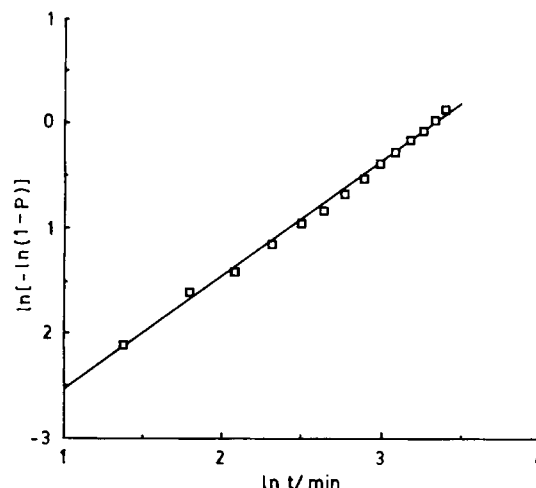
The Order of Reaction With Respect to Crosslinker and Catalyst Concentrations

To determine the order of reaction with respect to OR group concentration, values of ln k_1 (Table I) were plotted against ln[OR]$_\circ$. This plot as shown in Figure 7 shows reasonable linearity with a slope of unity up to about 7 g/L of alkoxy groups. The slope of the straight line gave the order of reaction with respect to [OR] of 0.95. The order of reaction with respect to tin concentration was determined using the same approach as used for [OR]$_\circ$ group variation. The values of log k_1 (Table I) were plotted versus log[Sn]$_\circ$ (Fig. 8). This plot is a fair straight line the slope (about 0.24) which gives the order of reaction with respect to tin concentration.

Table I Effect of Variation of Crosslinker and Catalyst Concentration on the First-Order Rate Constant

Crosslinker Variation			Catalyst Variation		
[OR]$_\circ$ (g/L)	[Sn]$_\circ$ (g/L)	K1	[Sn]$_\circ$ (g/L)	[OR]$_\circ$ (g/L)	K1
0.645	0.172	0.004	0.034	2.149	0.0052
1.186	0.172	0.0075	0.049	2.148	0.008
1.69	0.173	0.0118	0.077	2.148	0.0084
2.816	0.172	0.019	0.086	2.148	0.0088
6.008	0.171	0.0338	0.209	2.147	0.0107
7.182	0.171	0.0328	0.371	2.146	0.0123
15.855	0.169	0.0304	0.889	2.142	0.0136
21.147	0.168	0.0328	1.693	2.135	0.0159
26.599	0.167	0.028	5.994	2.099	0.0208
32.23	0.166	0.026	10.04	2.065	0.0168
36.142	0.165	0.0267	13.18	2.039	0.0176
40.64	0.164	0.0184			
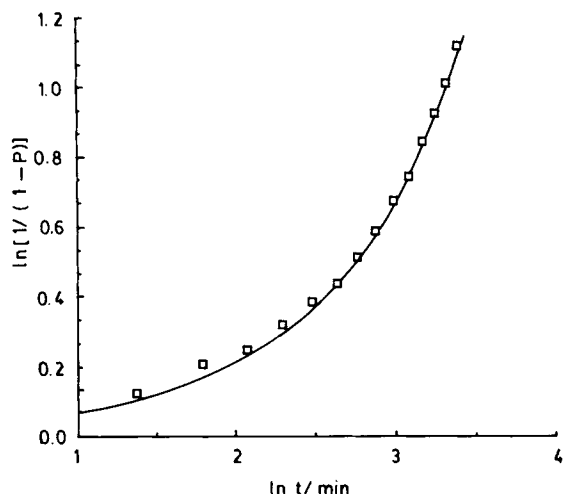
Figure 6 Plot of data for curing of HOPDMS according to second-order rate (log form) equation.

Figure 7 Variation of $K1$ with $[OR]_\circ$ of crosslinker.

DISCUSSION

Kinetics of Polycondensation of HOPDMS

The plots needed were drawn in terms of g/L of the respective groups instead of mol/L because of the unknown molecular weight of the prepolymer. It was the concentration of these reactive species in the compounds that mattered and not the compounds themselves. In the light of the different proposed mechanisms[7,8] for crosslinking, it seems that the tin (Sn) in the organotin compound is somehow more important than the ligands for the reaction. So for determining the order of reaction with respect to catalyst, the tin concentration in the compound was considered.

Though the uncertainty (± 5 mV) in the value of V_α (i.e., 44 mV) is unfortunate, its effect on the data was comparative and therefore not too significant when the extent of reaction was calculated. A single value V_α was used for all the calculations on the assumption that the OH groups of HOPDMS react only with the alkoxy groups of crosslinker and the standard amount (15 g) of prepolymer was used in all experiments contained fixed number of potential crosslinking points available.

Although the data deviated slightly from linearity of the first-order rate equation after about 16 min, it was the initial period of reaction that was important. Moreover, the fact that crosslinking of HOPDMS is moisture sensitive[9,10] makes this reaction to be diffusion controlled at the latter stages. Most of these $\ln[1-p]$ versus t plots extrapolated to a value of $[1-p]$ close to unity, which suggest that there is no induction period after mixing cat-
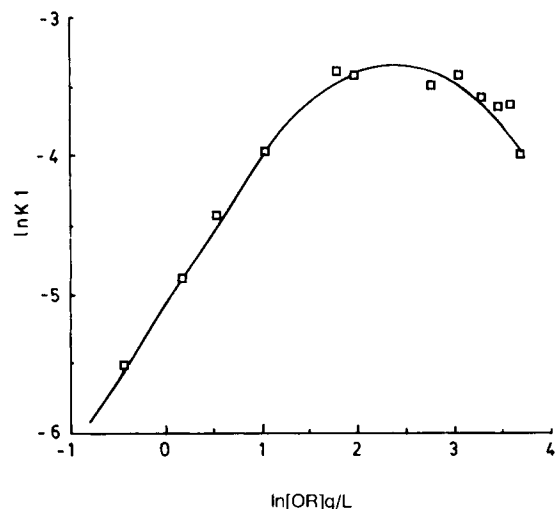
alyst and crosslinker with HOPDM. Nudel'man and other investigators[1,11,12] have also concluded that there is no induction period for this reaction.

Variation in $[OH]_\circ$ was not possible by using different molecular weight prepolymers for the crosslinking reaction, because the concentration of OH groups along the chain was found to be constant.[6]

The Order of Reaction With Respect to Crosslinker and Catalyst Concentrations

The order of crosslinking reaction with respect to OR group concentration is close to unity. The reaction followed this order of unity up to about 7 g/L of OR groups (Fig. 7). For higher than 7 g/L of OR groups, the initial rate of reaction dropped (Table I). These higher concentrations of crosslinker
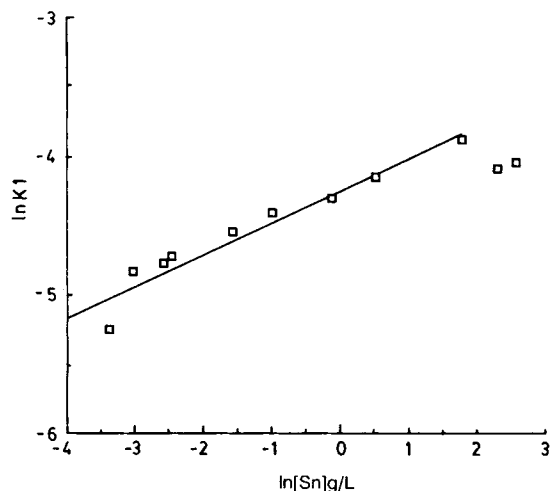

Figure 8 Variation of $K1$ with $[Sn]_\circ$ of catalyst.

were studied to establish its limit of concentration control of the rate of the crosslinking for the given mixture.

In the case of catalyst variation for constant amounts of HOPDMS and crosslinker, the plots of log of reaction rate versus log of catalyst concentration were linear up to about 7 g/L in Sn (Fig. 8). The order of reaction with respect to catalyst concentration, $z = 0.24$, obtained is interesting. The published values of z vary between 0.5 and 1.[3,13] The limit of concentration control of rate of crosslinking is at $[Sn]_\circ = 7$ g/L.

The observation of having no activation energy for polycondensation reaction is in accordance with the usual consideration of silicone as room temperature vulcanisates.

CONCLUSIONS

The VNC can be used to give an indication of the kinetics of the curing process, which for the system studied are in good agreement with what sparse information is available in the literature.

Furthermore, although the VNC has been previously reported to be effective in following the course of a reaction, such as the curing of polyurethane, it failed to allow a rigorous evaluation of the kinetics of the polycondensation of silicones. However, it is an inexpensive instrument, with much application potential and allowed a determination of

the order of the polycondensation that was not very different from the model compounds previously reported.

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