

Curing Reactions and Modeling of Silicone–Carbon Resins

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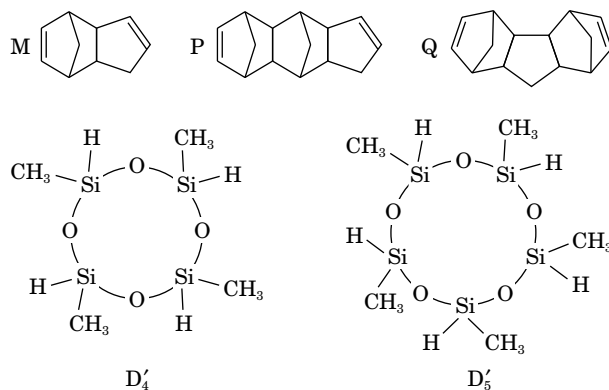
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ABSTRACT: New silicone–carbon resins have been made, based on four- or five-membered cyclosiloxanes, cyclopentadiene dimer (DCPD), and cyclopentadiene trimer (TCPD). The monomers are first polymerized to a B-stage resin, and then heated at higher temperatures to cure. In this work, the curing reaction of this silicone–carbon resin (which leads to network formation) is simulated using two approaches. In the first approach (stochastic model), all the available functional groups (olefin and silyl hydride) are allowed to react with each other with equal probability. This gives the kinetically controlled, liquidlike, diffusion-free limit. Extrapolation of the model to reactions where diffusion may play a role can be made by including molecular weight dependence in the rates. This dependence on the molecular weight can be scaled to fit the experimental data. In the second approach a percolation model is used. In the extreme case, this model corresponds to the solid-state reaction between silicone–carbon resin molecules on 2-dimensional or 3-dimensional rigid lattices. Relaxation of this geometric constraint can be made by providing a larger reacting distance between the reactants. Computer programs have been written for 2- and 3-dimensional lattices. Illustrative examples are given for these approaches. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1557–1573, 1997

INTRODUCTION

Recently the preparations of new silicone–carbon resins have been reported.^{1–11} These resins have good mechanical and dielectric properties and may find application as composite matrices, high-performance adhesives, and electronic materials. The resins are made from methylhydrocyclosiloxanes (MHCS) consisting of four- or five-membered cyclosiloxanes (D'_4 and D'_5 , respectively), cyclopentadiene dimer (DCPD or M), and optionally cyclopentadiene trimer (TCPD, in two isomers P or Q).

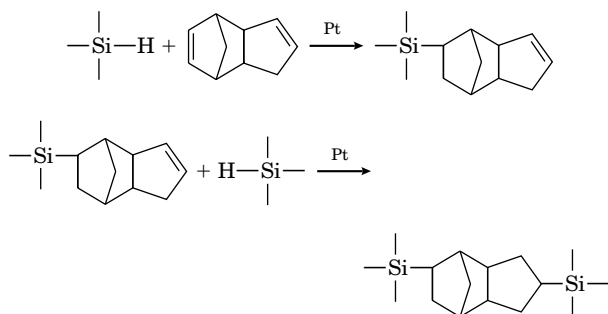


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The polymerization depends on Pt-catalyzed hydrosilylation reaction^{12,13} whereby an olefin is added to the silyl hydride, for example,



In the above reaction the norbornene double bond of DCPD is shown to have reacted first because the norbornene double bond is more reactive than the cyclopentene double bond.

Two types of resins have been synthesized: type 1 composed of MHCS and M only, and type 2 comprising MHCS and a mixture of M , P , and Q . The reactants are polymerized such that 52% of the combined olefins in DCPD reacted. The product is used as the B-stage resin, in which most of the norbornene double bond (and a few percent of the cyclopentene double bond) reacted. The B-stage resin is a liquid polymer and can be readily incorporated in an end product. The product is then thermally cured to promote further hydrosilylation such that the silicone-carbon resin forms a thermoset.

Earlier we reported^{14,15} on approaches to simulate the polymerization of the B-stage resin. Molecular weight distribution, substitution pattern on the cyclosiloxane ring, and extents of reaction of M , P , and Q can be obtained as a function of

time or conversion. Because the end use of these resins requires them to be cured at higher temperatures, it would be desirable to have computer approaches that can simulate the curing reaction of these silicone-carbon resins. This simulation is the subject of this work.

RESULTS AND DISCUSSION

We approach this problem from two directions. In the first approach (stochastic model), we assume that the curing reaction occurs mostly in the liquid state and allow all reacting functional groups to react until gelation is reached. Near gelation, the reaction rate of a particular molecule is scaled down according to its molecular weight to reflect the increased viscosity. In the second approach, we treat the system as a solid lattice using a percolation model.

In either approach, gel point can be determined by plotting weight-average molecular weight (M_w) as a function of conversion. At the gel point, M_w should increase rapidly. A better measure of gel point was suggested by Hoshen and Kopelman,¹⁶ Shy et al.,¹⁷ and Gupta et al.¹⁸ As the chains are reacted, a certain amount of small polymers are formed, and some large polymers are also formed. Because the large polymers have more reacting groups, they grow faster. Invariably, near the gel point one large macromolecule tends to show up incorporating a large number of available chains in the computer pool. This one

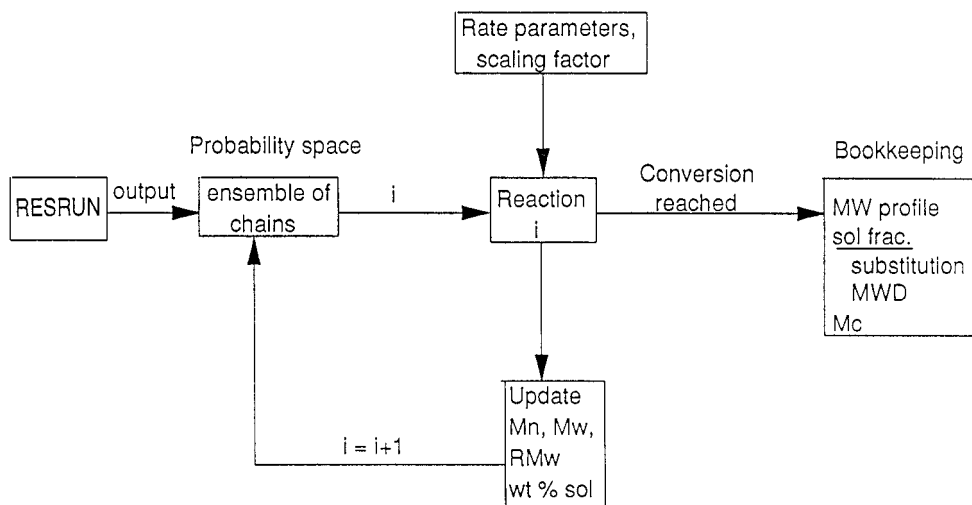


Figure 1 Logic diagram for program RESCURE1 (the stochastic model).

macromolecule can unduly distort the M_w . For this reason, "reduced molecular weight" has been defined¹⁶⁻¹⁸ as the M_w of all molecules *excluding* this largest molecule. If we plot the reduced molecular weight versus conversion, we would see a maximum at the gel point.

Another useful parameter is M_c , the average molecular weight of polymer chain segments between crosslinking points.¹⁹ This value in effect provides the "mesh size" of the network. The M_c is useful in elastomeric networks because many

physical properties depend on it.²⁰ For future reference, we have provided an estimate of M_c from the results of the simulations.

Stochastic Model

In this model we use the Monte Carlo procedure²¹⁻²⁵ to "react" the MHCS structure with DCPD and TCPD. Two rate parameters characterize the reactivities of norbornene and cyclopentene double bonds (k_1 and k_2 , respectively). A first

Table I Input Parameters to Program RESCURE1

Parameters							
Fraction of $D_4 = 5.555556E-01$							
$K_4 = 1.000000$							
$z_{12} = 2.500000E-01$				$e_{12} = 4.500000E-01$			
$z_{13} = 2.500000E-01$				$e_{13} = 4.500000E-01$			
$K_5 = 1.000000$							
$z_{12} = 4.000000E-01$				$e_{12} = 4.500000E-01$			
$z_{13} = 4.000000E-01$				$e_{13} = 4.500000E-01$			
$k_1 = 100.000000$							
$k_2 = 1.000000$							
[SiH rings] = 1.000000				[DCPD] = 2.222222			
Mol. frac. $M = 1.000000$				Mol. frac. $P = 0.000000E+00$			
Mol. frac. $Q = 0.000000E+00$							
Percent DCPD/TCPD added per step = 2.002700							
No. rings in system, = 2000 %				Conversion = 53.117970			
Results							
Substitution on Silicon Rings (%)							
	0	Mono	Di	Tri	Tetra	Penta	Functionality
D_4	0.00	10.44	65.26	23.76	0.54	0.00	2.14
D_5	0.00	2.81	41.39	46.23	9.22	0.34	2.63
Total	0.00	7.05	54.65	33.75	4.40	0.15	2.36
M (%)							
Unreacted = 5.76							
Monosubst. = 82.31							
Disubst. = 11.93							
P (%)							
Unreacted = 0.00							
Monosubst. = 0.00							
Disubst. = 0.00							
Q (%)							
Unreacted = 0.00							
Monosubst. = 0.00							
Disubst. = 0.00							
$M_n = 740$			$M_w = 920$		$M_w/M_n = 1.31$		
Percent area with MW > 950 = 18.4							

Parameters were obtained as the output of the earlier program, RESRUN.FOR.¹⁴

reaction of DCPD or TCPD on the cyclosiloxane ring (D'_4 or D'_5) slightly disfavors the remaining silyl hydrides on the ring toward further reaction, and correction factors need to be used on the rate parameters for successive reactions on the same ring. This model is thus related to the program RESRUN.FOR that was reported previously¹⁴ for the simulation of the B-stage resin.

For simplicity, this model uses the output from program RESRUN.FOR. The output (corresponding to the B-stage resin) consists of an ensemble of polymer chains with a specific MHCS substitution pattern and molecular weight distribution.¹⁴ In the curing reaction these chains are allowed to react further. New reaction constants may be used to reflect the higher temperature of the curing reaction. Again, the Monte Carlo process is used to decide which chains are to be reacted.

In a freely reacting (kinetically controlled) reaction, all chains irrespective of molecular size have the same probability of reaction. At a specific degree of conversion, we can monitor the weight average molecular weight, the sol fraction (arbitrarily defined to be those chains less than 50,000 in molecular weight), the molecular weight distribution, and the MHCS substitution pattern in the

sol fraction. In addition, the reduced molecular weight and M_c are calculated.

In most network formations, the polymer solution becomes viscous near the gel point. The reaction then becomes less kinetically controlled and more diffusion controlled. In this domain (typically within 5–8% of the gel point) the freely reacting model may produce less satisfactory results. We can correct for this effect by considering the viscosity (η) effect on the rates. For a branched polymer (molecular weight exceeding 2 or 3 times M_c), $\eta \propto \exp(M_w)$. For simplicity, we treat the rate as an arbitrary function of M_w ,

$$\text{rate} \propto M_w^{-a} \quad (1)$$

where M_w is the weight-average molecular weight of a given chain and a is an adjustable parameter that is used to scale down the reaction rate. In the general case, a is dependent on conversion (ν)

$$a = a_0 + a_1\nu^{a_2} \quad (2)$$

For the freely reacting model, $a_1 = 0$. By varying the values of a_i , we can use the stochastic model to obtain a match with the experimentally observed data

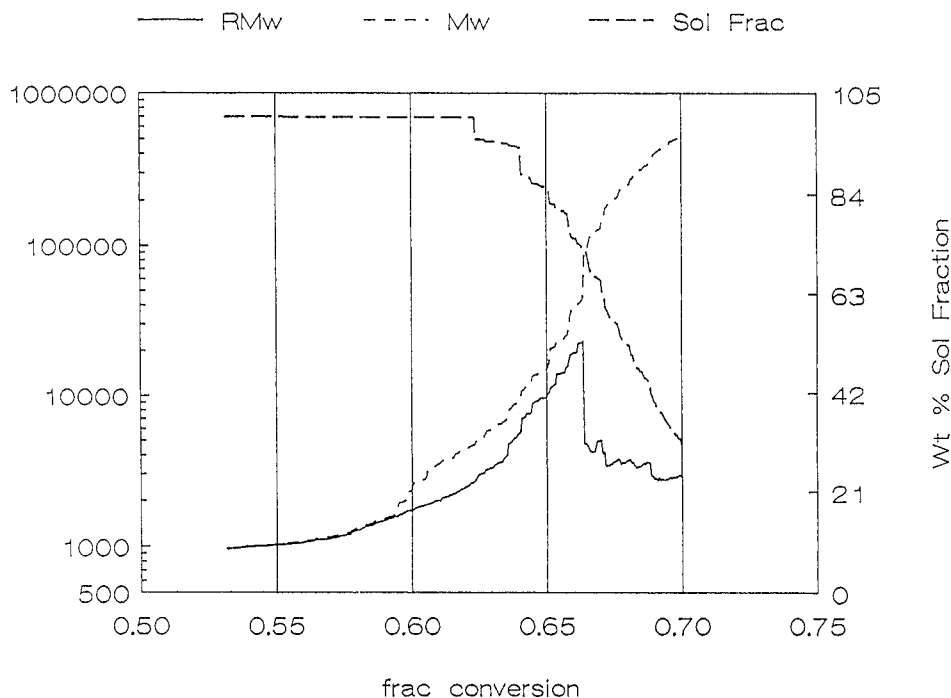


Figure 2 Gelation plot as simulated through program RESCURE1 ($a_0 = 0$). RM_w : reduced weight average molecular weight.

Table II Output of Program RESCURE1

Parameters							
Fraction of D ₄ = 5.555556E-01							
K ₄ = 1.000000							
z ₁₂ = 2.500000E-01				e ₁₂ = 4.500000E-01			
z ₁₃ = 2.500000E-01				e ₁₃ = 4.500000E-01			
K ₅ = 1.000000							
z ₁₂ = 4.000000E-01				e ₁₂ = 4.500000E-01			
z ₁₃ = 4.000000E-01				e ₁₃ = 4.500000E-01			
k ₁ = 100.000000							
k ₂ = 1.000000							
[SiH rings] = 1.000000				[DCPD] = 2.222222			
Mol. frac. M = 1.000000				Mol. frac. P =			
Mol. frac. Q = 0.000000E+00				0.000000E+00			
Viscosity (micro): $\eta = K \cdot M_w \cdot (a_0 + a_1 \hat{v} + a_2)$							
K = 1.000000				a ₀ = 0.000000E+00			
Transition MW = 1.000000E+30				a ₁ = 1.000000E+30			
				a ₂ = 0.000000E+00			
Percent conversion = 70.002250							
Weight percent of sol fraction = 31.211060							
	<i>M_n</i>		<i>M_w</i>				<i>M_w/M_n</i>
Total	4035		527913				130.83
Substitution on Silicon Rings in Sol Fraction (%)							
	0	Mono	Di	Tri	Tetra	Penta	Functionality
D ₄	0.00	0.18	26.73	63.10	9.99	0.00	2.83
D ₅	0.00	0.00	2.81	51.63	42.29	3.26	3.46
Total	0.00	0.10	16.10	58.00	24.35	1.45	3.11
Distribution of DCPD/TCPD in sol fraction (MW < 50,000)							
M (%)							
Unreacted = 0.00				Total % M = 100.00			
Monosubst. = 60.07							
Disubst. = 39.93							
P (%)							
Unreacted = 0.00				Total % P = 0.00			
Monosubst. = 0.00							
Disubst. = 0.00							
Q (%)							
Unreacted = 0.00				Total % Q = 0.00			
Monosubst. = 0.00							
Disubst. = 0.00							

(e.g., M_w vs. conversion curve). In addition, a transition molecular weight (M_t) may be imposed such that before the M_t , the reaction follows the free reacting model, and after M_t the reaction is scaled.

A computer program incorporating the above ideas has been written and is called RESCURE1. A logic diagram of this program is given in Figure 1.

As an example of how this approach works, we

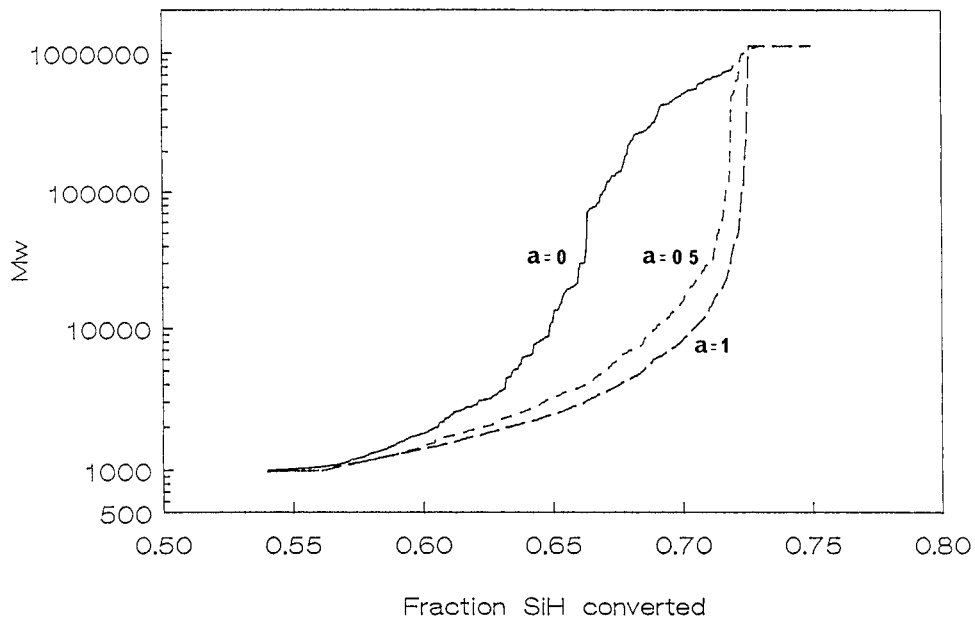


Figure 3 Gelation plot as a function of the exponent a_0 in eq. (1) (rate $\propto M_w^{-a}$). Simulation obtained through program RESCURE1.

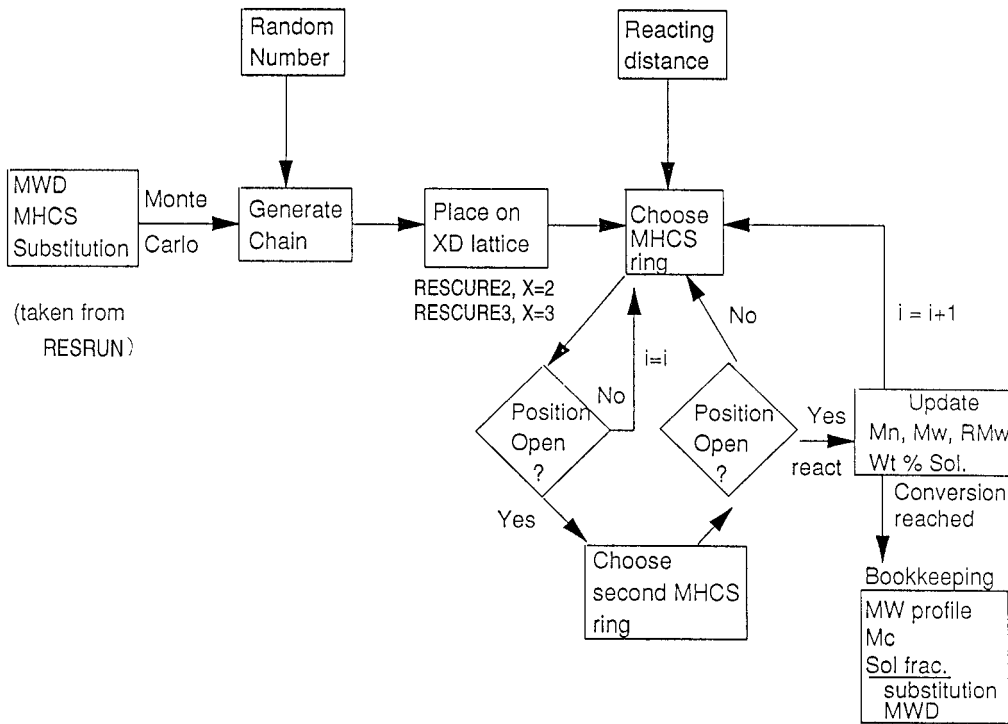


Figure 4 Logic diagram for program RESCURE2 (the percolation model).

Table III Input Parameters to Program RESCURE2

Parameters Used							
Fraction of $D_4 = 5.555556E-01$							
$K_4 = 1.000000$							
$z_{12} = 2.500000E-01$							$e_{12} = 4.500000E-01$
$z_{13} = 2.500000E-01$							$e_{13} = 4.500000E-01$
$K_5 = 1.000000$							
$z_{12} = 4.000000E-01$							$e_{12} = 4.500000E-01$
$z_{13} = 4.000000E-01$							$e_{13} = 4.500000E-01$
$k_1 = 100.000000$							
$k_2 = 1.000000$							
[SiH rings] = 1.000000							[DCPD] = 2.222222
Mol. frac. $M = 1.000000$							Mol. frac. $P = 0.000000E+00$
Mol. frac. $Q = 0.000000E+00$							
Percent DCPD/TCPD added per step							
= 4.960495E-01							
No. rings in system, = 2000							
Percent conversion = 50.022510							
Results							
Substitution on Silicon Rings (%)							
	0	Mono	Di	Tri	Tetra	Penta	Functionality
D_4	0.00	18.45	63.01	18.00	0.54	0.00	2.01
D_5	0.00	4.95	47.02	41.96	6.07	0.00	2.49
Total	0.00	12.45	55.90	28.65	3.00	0.00	2.22
M (%)							
Unreacted = 9.27							
Monosubst. = 81.46							
Disubst. = 9.27							
P (%)							
Unreacted = 0.00							
Monosubst. = 0.00							
Disubst. = 0.00							
Q (%)							
Unreacted = 0.00							
Monosubst. = 0.00							
Disubst. = 0.00							
$M_n = 671$ $M_w = 829$ $M_w/M_n = 1.23$							
Percent area with MW > 950 = 13.6							

Parameters were obtained as the output of the earlier program, RESRUN.FOR.¹⁴

take a typical output from program RESRUN.FOR (Table I). The information has been stored in a file called SCDAT i , where i is the run number. The program RESCURE1 can retrieve this file directly in a disk. Typically, 2000 MHCS rings are used in the simulation. If less than 2000 rings have been used in program RESRUN.FOR, some of the rings are randomly duplicated to bring the number up to 2000.

The input includes the percent conversion needed and the rate parameters for the curing reactions. Furthermore, the scaling factors (K , a_0 , a_1 , a_2) should be specified. The program will run automatically without further effort from the user. It will give the following information:

1. plot of M_w and the reduced molecular weight as a function of conversion, up to the speci-

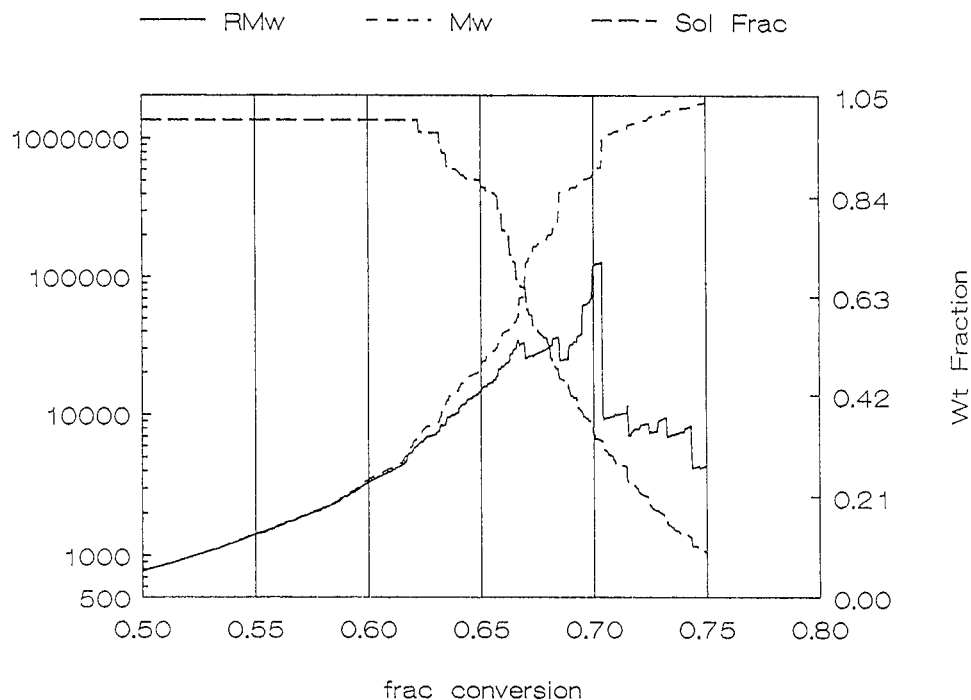


Figure 5 Gelation plot as simulated through program RESCURE2 ($R = 2$). RM_w : reduced M_w .

fied conversion level. The weight fraction of the sol fraction can also be superimposed on the curve.

2. Information on sol fraction at a specified conversion:
 - a. molecular weight distribution,
 - b. substitution pattern on the ring, and
 - c. distribution of norbornene/cyclopentene reactions in DCPD/TCPD moieties.

For illustration we use the same relative kinetic parameters for curing as in the B-stage resin. For simplicity, we work with type 1 resin and the free reacting model (i.e., $K = 1$, $\alpha_0 = \alpha_1 = 0$). The plot is shown in Figure 2. In this case, M_w rises quickly between 63 and 68% conversion. The reduced molecular weight gives a good measure of the gel point, which appears to be at 66% conversion. The sol fraction decreases very fast near the gel point. At 70% conversion it is 31% by weight.

A printout of the result of 70% conversion is given in Table II. The ring substitution pattern indicates that the sol fraction has a higher functionality than the B stage. As expected, a much higher level of the DCPD is now disubstituted.

Another useful illustration is to see the effect of different scaling factors. Let $K = 1$, $\alpha_1 = 0$, and vary α_0 from 0 to 1. Three plots are shown in Figure 3. The left plot (K independent of molecular weight) is the freely reacting model similar to Figure 2. The two other plots give the molecular weight dependence: $k \propto M^{-0.5}$ and $k \propto M^{-1}$. It is clear that as the scaling factor becomes more negative, the gel point becomes sharper. The maximum gel point using the B-stage relative rate parameters appears to occur at about 72% conversion.

Percolation Model

Percolation is a well-known concept²⁶ that has been used in network formation theories.^{18,27,28} In this work we follow a simplified algorithm proposed by Gupta et al.¹⁸ One difference is that Gupta et al. placed their groups *off* lattice, whereas in this work we placed our groups *on* lattice. A logic diagram is given in Figure 4.

The silicone-carbon resin system with all the isomers and the multiple components is too complex to treat by these means. Some simplifying assumptions are needed as given below:

Table IV Output of Program RESCURE2

Input Parameters					
MHCS distribution (mol %)					
$D_{41} = 18.450000$		$D_{51} = 4.950000$			
$D_{42} = 63.010000$		$D_{52} = 47.020000$			
$D_{43} = 18.000000$		$D_{53} = 41.960000$			
$D_{44} = 5.400000E-01$		$D_{54} = 6.070000$			
DCPD distribution (mol frac)					
1 end = 8.978000E-01		Both ends = 1.022000E-01			
Reaction parameters					
Reaction dist (R) = 2.000000					
Fraction of $D_4 = 5.555556E-01$					
Ave MW DCPD/TCPD = 132.100000					
Max MW sol frac = 50000.000000					
Results					
Percent conversion = 75.005190					
Weight percent of sol fraction = 9.517319					
	M_n	M_w	M_w/M_n		
Sol fraction	1030	4352	4.23		
MHCS Distribution in Sol Fraction					
	Mono	Di	Tri	Tetra	Penta
D_4	13.79	40.52	27.59	18.10	0.00
D_5	4.40	31.45	38.99	16.35	8.81
Total	9.97	36.83	32.23	17.39	3.58

- There is no unreacted MHCS in the system:
- There is no pentasubstituted MHCS initially present in the system.
- All SiH groups have equal reaction probabilities (no substitution effects).
- Unreacted DCPD and TCPD are not present in the system.
- The norbornene and cyclopentene double bonds are equal in reactivity. (The program keeps track of whether DCPD is reacted at one double bond or at both double bonds.)
- The Monte Carlo process is used to recreate the system based on user-specified MHCS and DCPD/TCPD distributions.
- The reaction distance of a group is independent of the size of the chain where the group is located. In effect, we assume that each reacting group is a point in the lattice. Note that in this work we place the group on the lattice. This is distinct from the article by Gupta et al.,¹⁸ who placed their groups off lattice.
- The reaction cannot take place diagonally along the lattice. It can only be located vertically or horizontally along the Cartesian coordinates.
- The groups on the edge of the lattice can react with the groups on the opposite edge. This is needed to satisfy the periodic boundary conditions of the lattice. In addition, this allows all the groups on the lattice to have an equal number of neighbors.
- The molecular weight calculations use an average molecular weight of D'_4 and D'_5 and an average molecular weight of DCPD and TCPD species.
- The sol fraction is defined as the collection of chains whose members have molecular weights less than 50,000.

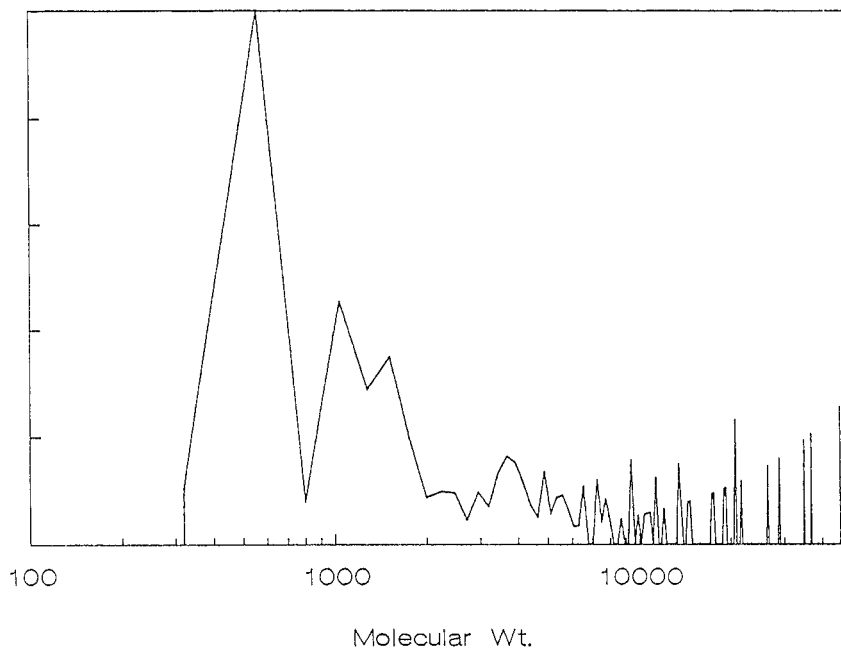


Figure 6 Simulated molecular weight distribution of toluene-soluble fraction for conversion at 67% (program RESCURE2).

A key point is that the ensemble of chains from program RESRUN.FOR is *not* used as input. Instead, the chains are regenerated from the available information of molecular weight distribution

and MHCS substitution. The chains are then placed on the 2-dimensional or 3-dimensional lattice (corresponding to program RESCURE2 or RESCURE3, respectively). Reactions are then al-

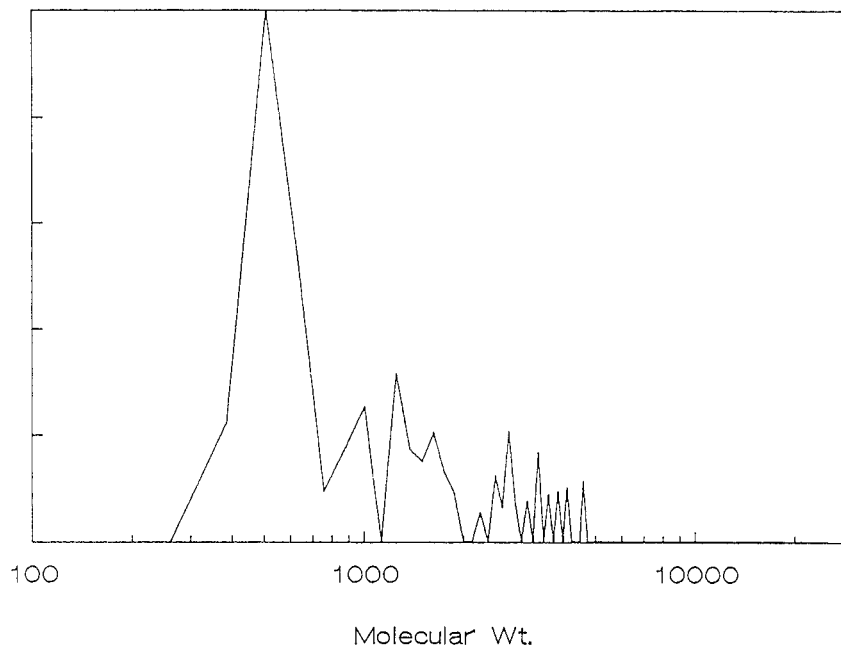


Figure 7 Simulated molecular weight distribution of toluene-soluble fraction for conversion at 75% (program RESCURE2).

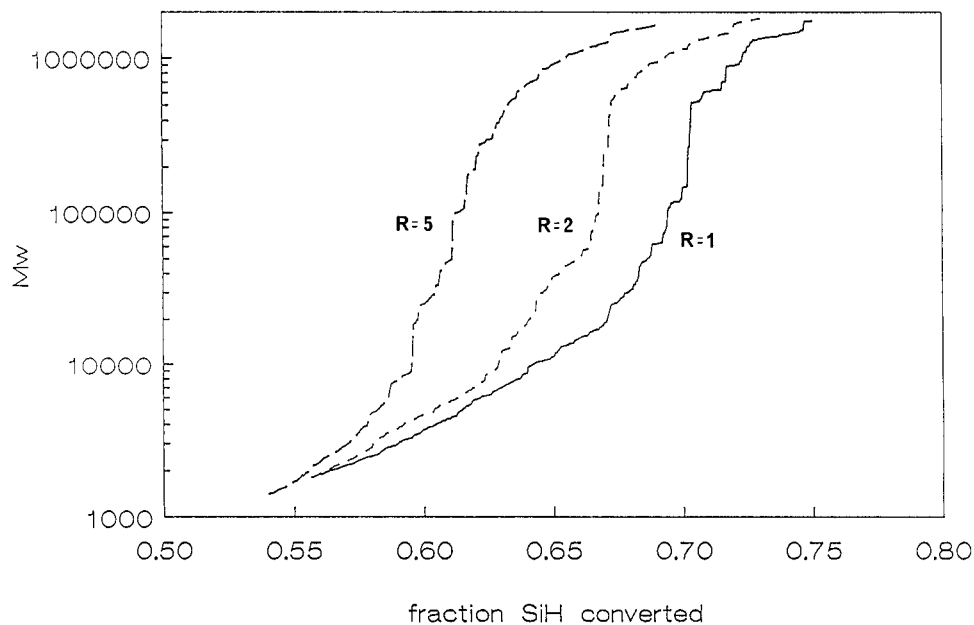


Figure 8 Gelation plot as a function of reaction distance (R). Simulation obtained through program RESCURE2.

lowed to proceed randomly between available pairs, assuming a certain distance. When the reaction distance is confined to the nearest neighbor, only immediately adjacent units can react. This would simulate either a solid-state reaction or a highly diffusion controlled reaction. An increase in the reaction distance would correspond to greater mobility of the reactants.

Examples are shown here of the use of programs RESCURE2 and RESCURE3. The inputs to these programs are given in Table III. The numbers are slightly different from those given in Table I. The user must take the information from Table III and then manually enter the MHCS substitution pattern and DCPD/TCPD distribution. In this case, no additional rate parameters are needed. The only parameter controlling the rate is the reacting distance.

Reaction Distance (R)	No. Neighbors	
	RESCURE 2	RESCURE 3
1	4	6
2	8	12
5	12	18

When the conversion is entered, the program will run by itself without further input from the user.

For program RESCURE2 and $R = 2$, the M_w

versus conversion plot is given in Figure 5. Again M_w rises very fast near the gel point. The reduced M_w indicates that the gel point is broad, hovering around 66–70% conversion. A printout of this simulation is given in Table IV. At 75% conversion, the amount of the sol fraction is down to about 10%. More information has been obtained on the sol fraction by plotting its molecular weight distribution at two conversions (Figs. 6, 7). It is of interest that with increasing conversion past the gel point, the sol fraction actually gets narrower in the molecular weight distribution.

Another way to examine the percolation model is to vary the reacting distance. For program RESCURE2, this dependence is given in Figure 8. The value of $R = 1$ (nearest neighbor reaction only) corresponds to the extreme diffusion limit. The gel point is at about 72% conversion. As we relax the rigidity of the lattice (greater R), the gel point shifts to lower conversions. For future reference, the printout corresponding to $R = 5$ is given in Table V. It is of interest that the sol fraction decreases in molecular weight and polydispersity as the reaction distance increases. In addition, the substitution functionality also decreases.

A similar plot can be made for program RESCURE3 (Fig. 9). In the extreme diffusion limit, we assume that a silicone-carbon polymer mole-

Table V Output of Program RESCURE2

Input Parameters					
MHCS distribution (mol %)					
$D_{41} = 13.150000$	$D_{51} = 3.600000$				
$D_{42} = 62.700000$	$D_{52} = 47.870000$				
$D_{43} = 22.700000$	$D_{53} = 41.800000$				
$D_{44} = 1.440000$	$D_{54} = 6.520000$				
DCPD distribution (mol frac)					
1 end = 8.093000E-01		Both ends = 1.907000E-01			
Reaction parameters					
Reaction dist (R) = 5.000000					
Fraction of $D_4 = 5.555556E-01$					
Ave MW DCPD/TCPD = 132.100000					
Max MW sol frac = 50000.000000					
Results					
Percent conversion = 70.004240					
Weight percent of sol fraction = 10.387450					
	M_n	M_w	M_w/M_n		
Sol fraction	846	1312	1.55		
MHCS Distribution in Sol Fraction					
	Mono	Di	Tri	Tetra	Penta
4 Mem	11.76	54.20	23.53	10.50	0.00
5 Mem	6.70	44.69	31.84	13.41	3.35
Total	9.59	50.12	27.10	11.75	1.44

cule can react with any one of the *six* neighbors. (This may be an overestimate because of the size of the molecules.) In this case, the gel point for $R = 1$ is about 64% conversion. Increasing the mobility of the molecules (higher R values) shifts the gel point downward, as expected.

A final illustration can be made by comparing the results of four-membered versus five-membered MHCS rings. The results (for program RESCURE2, $R = 2$) are given in Figure 10. As expected, the ring size has a large effect on the gel point. In this specific case, D'_4 requires 7% more conversion before gelling.

Fitting Curing Data to Models

Because quantitative models for the curing reaction are available, it is possible to study the curing behavior of these resins and fit the data to the models. A set of silicone-carbon resin samples

carefully cured under controlled conditions has been prepared. Six curing times have been used at 150°C varying from 2 to 20 min (Table VI). Under these experimental conditions, gelation occurred at around 7 min. The samples were Soxhlet extracted with toluene and separated into toluene-soluble and toluene-insoluble fractions. The fractions were then analyzed for conversion by $^1\text{H-NMR}$ and for molecular weight distribution by size exclusion chromatography (SEC). The results of the analysis are summarized in Table VII. Note that substantial toluene-insoluble materials are found in samples 4, 5, and 6. The conversion in the table is the average of NMR results for both sol and gel. The SEC data reflect the molecular weights of only the soluble fractions.

A fair amount of work was carried out to use RESCURE programs to fit the observed data as given in Table VII. Separate discussions are given below on the use of stochastic and percolation models.

Program RESCURE1

In our earlier work¹⁴ we determined the relative rate constants for the hydrosilation reaction occurring in the preparation of the B-stage resins (70°C). Because the relative rate constants we used provide reasonable fits to all observable data, we consider them reasonably close to the actual values. In contrast to the reactions leading to the B-stage resins, the curing reaction is carried out at 150°C or higher temperatures. For our preliminary study, we assume that the *relative* rate constants are the same at 150°C as at 70°C.

In all simulations we use 2000 MHCS rings with the conversion covering the 50–80% range indicated in Table VII. The simulations are tedious and time consuming, and only the final results are presented here.

A key parameter in the simulation is to determine the cutoff molecular weight (MW) for the sol fraction. This cutoff MW is very sensitive to the sol content (wt % sol) and the molecular weight distribution of the sol fractions. If we assume that the experimental data in Table VII are accurate, then we can proceed with the calculations. After extensive simulation with programs RESCURE1 and RESCURE2, it appears that the best cutoff MW value is 35,000–50,000. We use 50,000 in this work.

Attempts have been made to change the exponent a in eq. (1) (i.e., rate $\propto M_w^{-a}$). The best fit with observed data is obtained by setting $a = 0.2$.

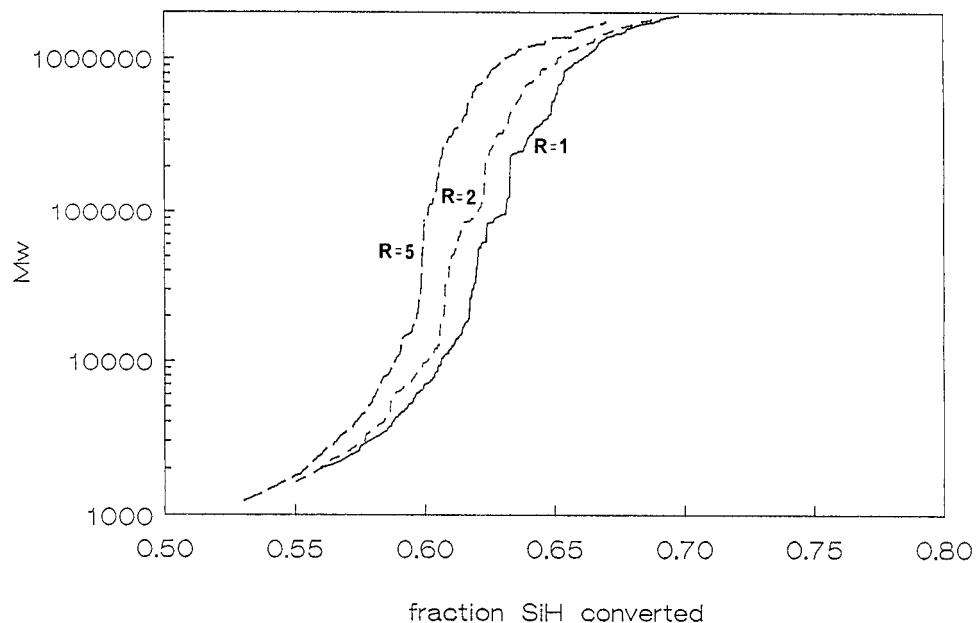


Figure 9 Gelation plot as a function of reaction distance (R). Simulation obtained through program RESCURE3.

This corresponds to a moderate diffusion constraint on the reaction rate as the molecular weight increases during curing. The gel point/conversion curve is given in Figure 11.

The sol content (dotted line in Fig. 11) de-

creases rather sharply past the gel point (at about 69% conversion). For comparison, the experimentally observed sol content is drawn as circles in Figure 11. The agreement is good below the gel point, but deviation becomes larger at conversions

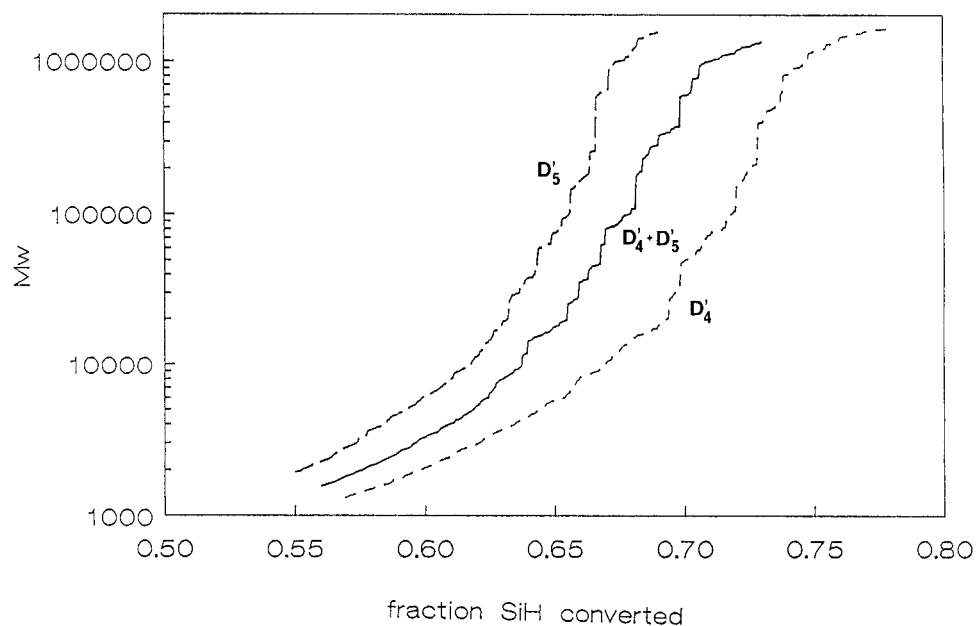


Figure 10 Gelation plot as a function of MHCS ring size. Simulation obtained through program RESCURE2.

Table VI Curing Study of Type 1 Resin at 150°C

Sample	Cure Time (min)	Weight Resin (g)			Time (h)	Soxhlet Extraction in Toluene				
		Before Cure	After Cure	Weight Loss (%)		Soxhlet Charge Weight (g)	Soluble		Insoluble	
							Weight (g)	%	Weight (g)	%
C1	2	6.06	6.05	0.17	4	6.05	6.03	99.7	—	—
C2	4	4.49	4.47	0.45	4	4.47	4.35	97.3	—	—
C3	6	6.07	6.04	0.49	4	6.04	6.00	99.5	0.03	0.5
C4	8	6.06	6.04	0.33	6	6.04	1.77	29.5	4.24	70.5
C5	10	6.07	6.05	0.33	6	5.65	0.74	13.1	4.90	86.9
C6	20	6.10	6.05	0.82	6	5.72	0.47	8.2	5.24	91.8

above the gel point. This is not unexpected because the stochastic model assumes a homogeneous reaction mixture. Beyond the gel point, the reaction becomes more constrained and may contain pockets of less reacted materials. If one were to play more with the variables a_0 and a_1 in Eq. (2), it may be possible to obtain a better fit with the experimental data.

The molecular weight moments and MHCS ring substitution patterns can be calculated separately using program RESCURE1. For two points above and below the gel point, the data are given in Table VIII. The observed values are also shown for comparison.

Program RESCURE2

We operate under the simplifying assumptions given earlier. A key feature is that the substitution effects on reactivity are ignored; thus, all Si—H groups are equally reactive. Moreover, it

is assumed that there is no residual DCPD; all DCPD molecules are assumed to have reacted. Thus, this model is suited only to the curing of the B-stage resin. As in program RESCURE1, we use a cutoff molecular weight of 50,000 for the sol fraction.

After a systematic study, we were able to get rather reasonable fits with the observed data. The reaction distance has to be increased to 2 (i.e., reaction with eight neighbors). The larger reaction distance reflects the mobility of the reactants near the gel point.

The simulated gel point/conversion curve is given in Figure 12. The calculated wt % sol and the observed wt % sol match fairly well. Even past the gel point (72% conversion), the predicted sol content gives reasonable agreement with the data. The good agreement in the postgel stage is an advantage of the percolation approach.

The simulated molecular weight values for two

Table VII Summary of Experimentally Observed Data on Type 1 Resin Cured to Different Extents

Sample	Cure Time (min)	Toluene Soluble (%)	Conversion (%)	SEC (Toluene Soluble)	
				M_n	M_w
Control	0	100	52	490	1810 ^a
1	2	99.7	54.7	570	1980
2	4	97.3	57.5	660	2430
3	6	99.5	68.4	1500	8450
4	8	29.5	73	(1120)	(7500)
5	10	13.1	73	(870)	(2990)
6	20	8.2	75	(830)	(2810)

Numbers in parentheses indicate the data for the soluble fraction only.

^a This number may be high due to the presence of a rubber additive.

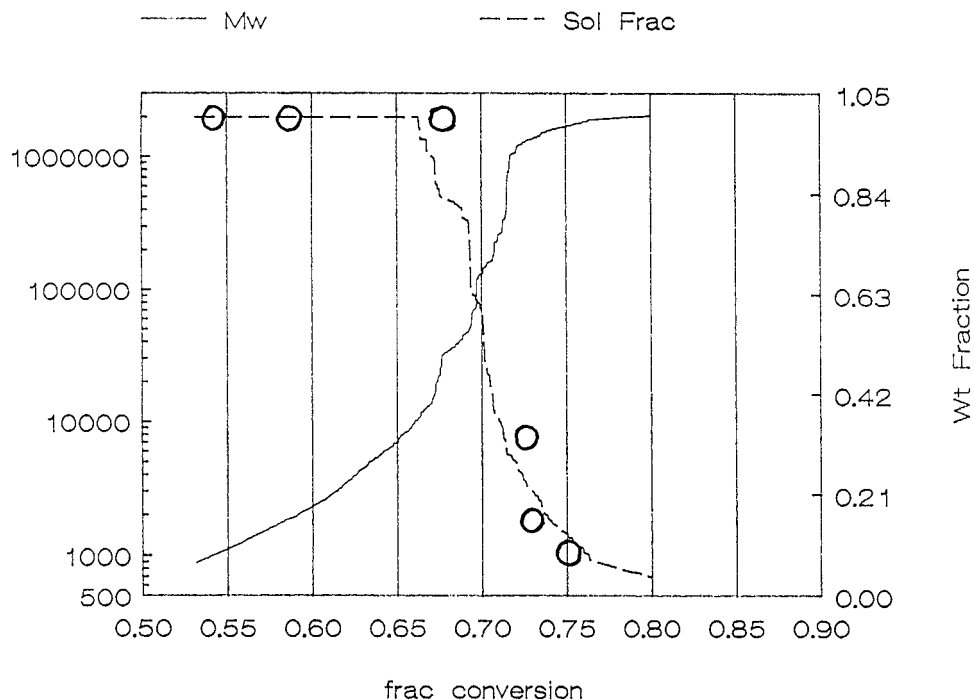


Figure 11 Simulation of the experimental data on cured type 1 resin. Gelation plot obtained through program RESCURE1. Lines refer to simulated results; circles refer to experimental points.

conversions above and below the gel point are given in Table VIII together with the observed values. The MHCS ring substitution pattern is

also included. The agreement between observed and calculated molecular weights is acceptable for this type of calculation. The substitution patterns

Table VIII Comparison of Experimental Molecular Weights and MHCS Substitution Patterns with Data Calculated with Programs RESCURE1 and RESCURE2

Molecular Weight Moments							
Sample	Conversion (%)	Observed		Calcd RESCURE1		Calcd RESCURE2	
		M_n	M_w	M_n	M_w	M_n	M_w
3	68.4	1500	8500	2450	8970	2000	10,100
5	73	870	2990	1520	2650	—	—
6	75	830	2800	—	—	1100	4800

Substitution Pattern on MHCS Rings										
Sample	Conversion (%)	Observed				Calculated				Program
		Mono	Di	Tri	Tetra+	Mono	Di	Tri	Tetra+	
3	68.4	3	32	43	21	0	20	58	22	RESCURE1
						4	30	37	30	RESCURE2
5	73	3	22	56	20	0	10	57	32	RESCURE1
6	75	3	19	58	20	5	40	34	21	RESCURE2

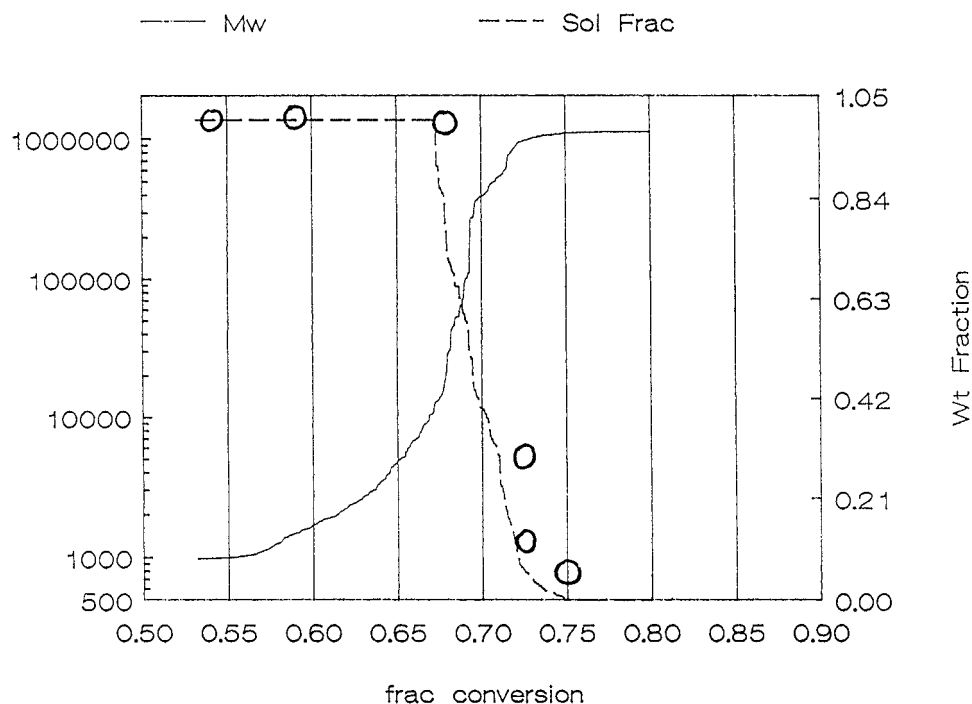


Figure 12 Simulation of the experimental data on cured Type 1 resin. Gelation plot obtained through program RESCURE2. Lines refer to simulated results; circles refer to experimental points.

are less accurate because of the assumption (viz., all Si—H having equal rate probabilities) used in the calculations.

EXPERIMENTAL

Computer simulation was carried out on an IBM 486/50 personal computer. All three programs (RESCURE1, RESCURE2, and RESCURE3) were written in Microsoft Fortran. The programs are self-contained with no external subroutine necessary. Plots were made using SlideWrite.²⁹

Molecular weights were determined using SEC. Conversion was determined from ¹H-NMR (for unreacted DCPD olefins) and through quantification of silyl hydride with a mercuric chloride procedure. For soluble polymer fractions, substitution patterns on the MHCS rings were determined through supercritical fluid chromatography and molecular weights by SEC.

CONCLUSION

In this work two computer approaches are used to simulate the curing reaction of the silicone-

carbon resins. Information available includes gel point, percent sol fraction at different degrees of curing, molecular weight distribution of sol fraction, and the polysiloxane ring substitution pattern in the sol and gel fractions. Three computer programs are available corresponding to these models. These programs have been used to fit the experimental data obtained on cured type 1 resins. For this system, the stochastic model is good up to the gel point. The percolation model gives a reasonable fit with the observed data above and below the gel point.

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