

Statistical Modeling and Monte Carlo Studies of Silicone–Carbon Resins

LEO J. KASEHAGEN, H. N. CHENG, PATRICK J. COWAN

Hercules Incorporated Research Center, 500 Hercules Road, Wilmington, Delaware 19808-1599

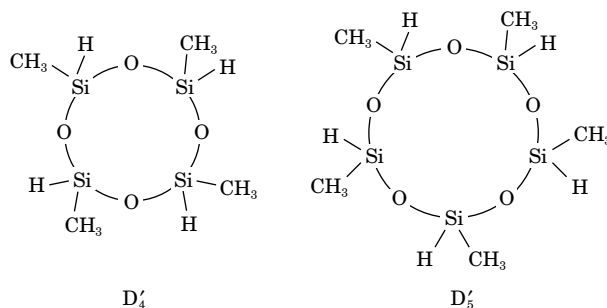
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ABSTRACT: The Pt-catalyzed hydrosilation reaction between methyl-substituted cyclosiloxane and a nonconjugated diene system produces silicone–carbon polymers with good mechanical and dielectric properties. In this work a statistical model is devised that provides a theoretical description of the polymerization reaction up to the B stage. An ensemble of cyclosiloxane molecules is built up in a computer and allowed to “react” with the diene (or mixture of dienes) in a Monte Carlo process. Included in the model are options for batch or semibatch operations. Through computer simulation, the concentrations of all molecular species at different conversions (as measured by the residual Si–H group) can be predicted as well as the molecular weight distribution. Good agreement is obtained with observed analytical data. The model is flexible and is used to study the effects of the changes in reaction process conditions on polymer structures and molecular weights. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 607–618, 1997

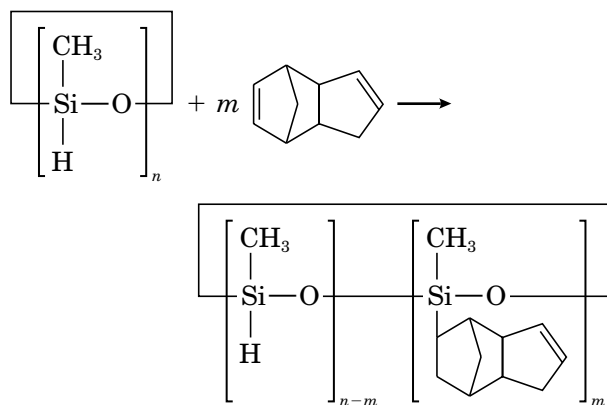
INTRODUCTION

A new class of silicone–carbon resins has been synthesized,^{1–11} based on the Pt-catalyzed hydrosilation reaction^{12,13} between a cyclosiloxane and a nonconjugated diene. The resulting polymer forms a B-stage resin that is useful as a matrix for composites, high-performance adhesives, or electronic materials. Upon thermal curing, the material becomes a thermoset that exhibits good mechanical and dielectric properties.

Currently, two types of resins have been made.^{1–3} Both types are based on methylhydrocyclosiloxane (MHCS), which is a 50/50 wt/wt mixture of tetramethylcyclotetrasiloxane (D_4') and pentamethylcyclopentasiloxane (D_5').



The Type 1 resin results from the Pt-catalyzed reaction between MHCS and dicyclopentadiene (abbreviated as DCPD, or M).

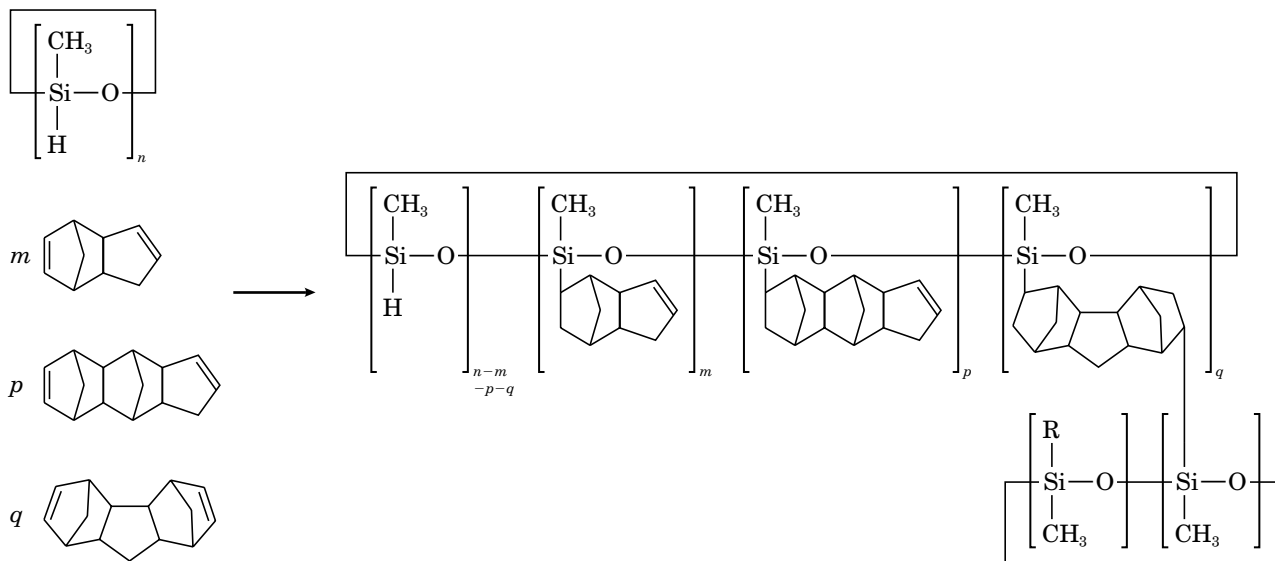


Correspondence to: H. N. Cheng.

Present address: L. J. Kauehagen, Department of Chemical Engineering and Material Science, University of Minnesota, Minneapolis, MN 55455.

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In the above reactions, DCPD can be multiply substituted on D'_4 and D'_5 . A variety of substitution products are formed, for example, mono-, di-, tri-, tetra-, and (for D'_5) penta-substitution. The resulting B-stage resin is a clear, flowing liq-



There are two trimers: nonsymmetric (P) and symmetric (Q), as shown above. The symmetrical trimer can readily form crosslinks that serve to increase the molecular weight of the B-stage resin, thereby improving tack properties of the resin.

Although the structures drawn above imply that the reaction affects only the norbornene double bond (bond 1), it is known that a small amount (up to 5%) of the cyclopentene double bond (bond 2) is also reacted at the B stage. The properties of the B-stage resin depend both on the substitution pattern on the MHCS and on the molecular weight distribution of the resin.

The process reported in the literature¹⁻¹¹ uses two reaction streams. MHCS is first placed in a reaction vessel (A side). A toluene solution of DCPD (and TCPD) and the platinum catalyst are prepared (B side) and added continuously over 1 to 2 h to the MHCS at 70°C. The reaction proceeds almost instantaneously. The reaction vessel is thermostated such that the heat generated in the reaction is removed.

Because the structures of the silicone-carbon polymers are complex, it would be desirable to use computer methods to simulate the polymerization. With an appropriate model, the experimen-

tal results can be predicted and compared with actual data. Modifications to the model can be made until a good fit is obtained between the observed and the calculated data. In this way, an improved understanding can be obtained of the relationship between the reaction process and the polymer structure. The model also provides a theoretical framework whereby the analytical data can be interpreted and interrelated.

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RESULTS AND DISCUSSION

Formulation of the Problem

The following experimental observations are useful in defining the problem: (1) DCPD is added to MHCS slowly in roughly 1-2 h. The reaction is very fast (on the order of seconds). (2) The temperature of the reaction is kept within a narrow range ($\pm 4^\circ\text{C}$). Thus, the temperature can be considered a constant for a given run. (3) At the B stage, DCPD reacts primarily through the norbornene double bond and secondarily through the cyclopentene. A realistic simulation requires specific inclusion of the reactions at both norbornene and cyclopentene double bonds.

In view of these considerations, we conceived

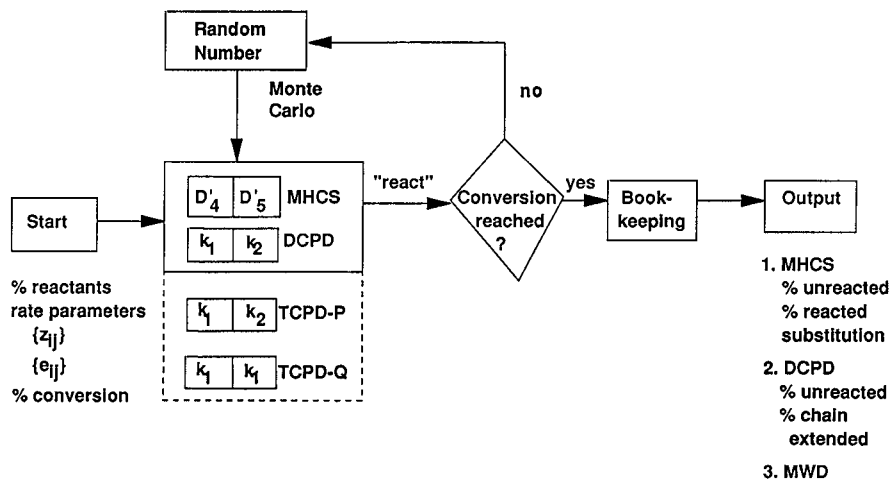


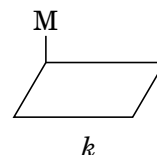
Figure 1 Scheme used in the simulation of silicone-carbon resins (program RE-SRUN.FOR).

an overall scheme as shown in Figure 1. In the input section, given amounts of MHCS and DCPD are combined. Two rate parameters are needed for the reaction of DCPD: k_1 (corresponding to norbornene reaction) and k_2 (corresponding to cyclopentene reaction). The MHCS in turn is composed of two components, D'_4 and D'_5 . The concentration of DCPD, D'_4 , and D'_5 can be varied by the user. The MHCS components (D'_4 and D'_5) require a set of rate parameters corresponding to mono-, di-, tri-, tetra-, and penta-substitution.

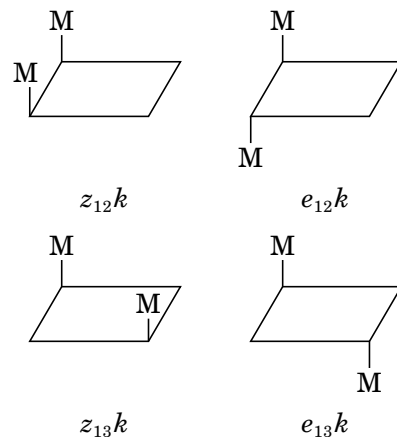
One way to express the rate parameters in terms of the degree of substitution is to use steric multiplicative factors. The scheme is shown below for D'_4 and DCPD and selected substitution patterns. If k is the rate parameter for the first substitution (to form a monosubstituted structure), then the rate parameters for di-substitution would be different (probably smaller) due to steric hinderance and other perturbations. For simplicity, we shall define four steric multiplicative factors: z_{12} = factor for 1,2-disubstitution in the Z configuration; e_{12} = factor for 1,2-disubstitution in the E configuration; z_{13} = factor for 1,3-disubstitution in the Z configuration; e_{13} = factor for 1,3-disubstitution in the E configuration.

The rate parameters for 1,2-disubstitution in the Z configuration is then $z_{12}k$ (where $z_{12} < 1$). Similar factors hold for the other substitution patterns. For tri-substitution, these steric factors are multiplied together as shown in the following scheme. Tetra-substitution follows the same logic.

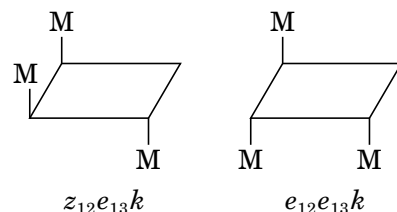
monosubstitution



disubstitution



trisubstitution



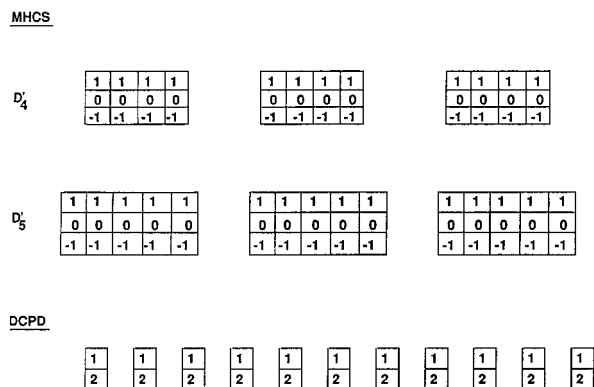


Figure 2 Probability spaces used for the organization of molecules in the simulation.

Similar consideration also holds for D'_5 ; again, four parameters are needed, designated as z'_{12} , e'_{12} , z'_{13} , e'_{13} .

The desired output should include all the information that can be measured analytically. These are: percent MHCS reacted and the substitution patterns, percent DCPD reacted through norbornene and through cyclopentene, and the molecular weight distribution (Fig. 1).

Statistical Model

In order to provide flexibility in changing polymerization conditions and stoichiometry, we have chosen the Monte Carlo simulation procedure.¹⁴⁻²⁰ In this methodology, the hydrosilation reaction is simulated in a computer, the reactivity being dictated by reaction probabilities that are proportional to the rates of the individual reactions. As many probabilities are used as there are reactions. A random number generator determines which reaction should occur at every step. The process is repeated until a given conversion is reached.

Type 1 Resin (MHCS Reacting with DCPD)

This is a moderately difficult problem in that two MHCS monomers are involved (D'_4 and D'_5), with different rate parameters relating to the substitution pattern. In addition, the DCPD monomer can react in two ways. To facilitate the programming effort, we organize the molecules in a probability space (Fig. 2). Each molecule of D'_4 or D'_5 is considered to be a cell, consisting of 12 or 15 compartments. The compartments are labeled 0, 1, or -1 corresponding to no substitution, substitution above, or substitution below the ring, respec-

tively. Before reaction, all compartments in D'_4 and D'_5 molecules have the same probability of reaction. Each compartment takes up the space of irrational numbers between 0 and 1. Thus, if there are n compartments altogether, each compartment takes up exactly $1/n$ space. A random number generator (producing an irrational number between 0 and 1) would pick any compartment at random for reaction. After one compartment has reacted, the probability space corresponding to that compartment is set to 0. Furthermore, the other compartments within the same molecule (cell) have to shrink corresponding to e_{ij} and z_{ij} values. Because the entire probability space needs to be filled up between 0 and 1, all other compartments (in the other cells) would expand slightly. The probability space is now ready for the reaction. The Monte Carlo process is started again, and the process is repeated.

Similar considerations hold for DCPD. Two compartments characterize each DCPD molecule, corresponding to k_1 and k_2 reactions. Depending on the relative magnitudes of k_1 and k_2 , compartments 1 or 2 would have different probabilities of being picked to react with MHCS.

In actual simulation, the Monte Carlo process is allowed to proceed until the desired conversion is reached. A bookkeeping exercise is then undertaken to count all the MHCS molecules (in terms of the substitution patterns), DCPD molecules (as to their reaction status), and the molecular weight distribution. The entire process is coded in a Fortran program called RESRUN.FOR. The information is stored in the hard disk and can be printed or displayed using a commercial graphics package.

Type 2 Resin (MHCS reacting with DCPD and TCPD)

In this case, two more comonomers (P and Q) must be incorporated in the probability space for DCPD. We assume for simplicity that all norbornene double bonds (1 bond in M, 1 in P, and 2 in Q) have the same reactivity, and all cyclopentene double bonds (1 bond in M and 1 in P) have the same reactivity. An advantage of the Monte Carlo process and the probability space concept is that the addition of these two comonomers (formally a very complex four-component copolymerization) does not unduly complicate the software. The Monte Carlo process remains unchanged. The only major changes occur when we carry out the

Parameters Used :

```

Fraction 4 member = 5.555556E-01
Si rings

K4 = 1.000000
z12 = 2.500000E-01    e12 = 4.500000E-01
z13 = 2.500000E-01    e13 = 4.500000E-01

K5 = 1.000000
z12 = 4.000000E-01    e12 = 4.500000E-01
z13 = 4.000000E-01    e13 = 4.500000E-01

k1 = 100.000000
k2 = 1.000000

[SiH rings] = 1.000000
[DCPD] = 2.222222

% CONVERSION = 52.408820
    
```

Results :

```

Functionality of Silicon Rings :
      0      Mono      Di      Tri      Tetra      Penta      Func.
-----
4 Mem      .00     11.89     63.96     23.42         .72         .00         2.13
5 Mem      .00      3.37     42.02     48.76         5.39         .45         2.58
Total      .00      8.10     54.21     34.69         2.80         .20         2.33

% Unreacted DCPD = 5.400540E-01
% DCPD reacted at both = 5.310531
double bonds
    
```

Mn = 652. Mw = 775. PD = 1.19

Figure 3 Output of the program RESRUN.FOR (for Type 1 resin).

bookkeeping procedure trying to determine the substitution, molecular weight distribution, and similar information. The computation has also been coded into program RESRUN.FOR.

Examples

The same program can be used for both types of silicone-carbon resins. Once the appropriate values for the rate parameters have been determined, various simulations can be made readily.

Type 1 Resin

For illustration, the following parameters are used:

Overall [DCPD] = 2.22 mol/L
 Overall [MHCS] = 1.00 mol/L

Mol % D₄' = 55.5%
 Mol % D₅' = 44.4%

Reaction mode = semi-batch addition of DCPD/
 catalyst to MHCS.
 Conversion = 52.4%

The program RESRUN.FOR allows for either batch or approximately "semibatch" reactions. In the "semibatch" reaction an option is provided to add the DCPD in large or small doses. The desired conversion is divided equally by this dosage rate. After every dose of DCPD, the reaction is allowed to proceed in the batch mode until the next dose is added (as dictated by the conversion requirement).

In an exploratory study, the gas chromatography data indicated that both D₄' and D₅' decay

Table I Substitution Patterns of the DCPD on the MHCS Rings, Observed^a vs. Calculated Values for Types 1 and 2 Resins at the B Stage (52% Conversion)

	Type 1 Resin (obsd)		Type 1 Resin (calc)		Type 2 Resin (calc)	
	D ₄ '	D ₅ '	D ₄	D ₅	D ₄	D ₅
Unsubstituted	0	0	0	0	0	0
Monosubstituted	13.1	6.5	11.9	3.4	12.3	2.9
Disubstituted	60.3	34.6	64.0	42.0	62.2	37.3
Trisubstituted	23.9	45.0	23.4	48.8	23.8	51.5
Tetrasubstituted	2.7 ^b	11.0 ^b	0.7	5.4	1.8	7.6
Pentasubstituted	—	2.9 ^c	—	0.5	—	0.7

^a Observed substitution patterns are only available from Type 1 resin; the SFC data from Type 2 resin are not fully deciphered.

^b High-molecular-weight species are also found here in the SFC data.

^c Estimated value.

with the same rate; thus, k_4 is approximately equal to k_5 . These are both set to 1 for convenience. The z_{ij} and e_{ij} parameters need to be varied to fit the model to the observed analytical data. After several iterations, it appears that the following parameters give good agreement:

For D₄'

$$z_{12} = 0.25, \quad e_{12} = 0.45$$

$$z_{13} = 0.25, \quad e_{13} = 0.45$$

For D₅'

$$z'_{12} = 0.40, \quad e'_{12} = 0.45$$

$$z'_{13} = 0.40, \quad e'_{13} = 0.45$$

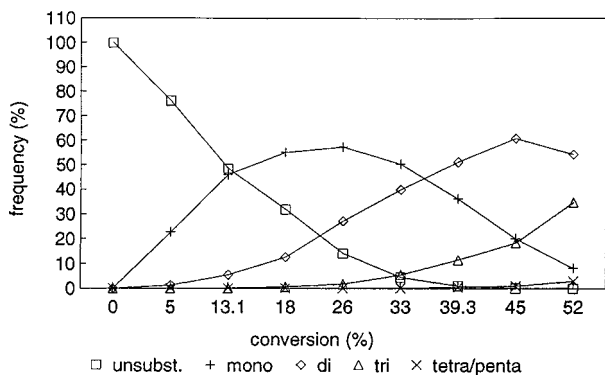


Figure 4 Substitution pattern (of DCPD) on the MHCS rings for Type 1 resins as a function of conversion, simulated through program RESRUN.FOR. The notations unsubst., mono, di, tri, tetra, penta refer to the unsubstituted rings, mono-, di-, tri-, tetra-, and penta-substitution, respectively.

In addition, DCPD needs to have the following rate parameters in order to fit the data. (In the actual computation, only the ratio k_1/k_2 is used.)

$$k_1 \text{ (norbornene reaction)} = 100$$

$$k_2 \text{ (cyclopentene reaction)} = 1$$

Using the above rate parameters, we readily obtain all the desired information. A printout of the RESRUN.FOR output is given in Figure 3. The simulated substitution patterns (for the B-stage resin) is shown in Table I, which compares favorably with the observed data (obtained from supercritical fluid chromatography, SFC).

Another way to study observed vs. calculated data is to predict the substitution pattern as a function of conversion. The predicted graph (Fig. 4) shows a fairly typical consecutive reaction kinetics plot. The shapes of the curves change when the kinetic parameters are altered.

Table II Observed and Calculated Molecular Weights for Type 1 Resin

Observed ^a			Calculated		
Conversion (%)	M_n	M_w	Conversion (%)	M_n	M_w
12.5	450	462	13	415	422
25	450	462	26	448	463
37.5	461	489	40	505	527
50	486	548	52	652	775

^a Determined by size exclusion chromatography, based on polystyrene standards. Values are approximate and are to be used on the relative basis only.

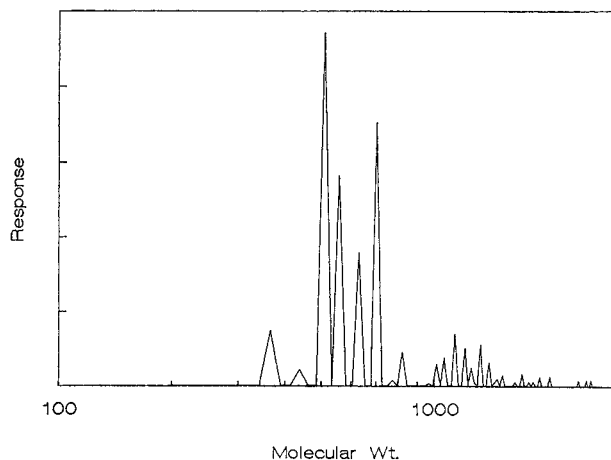


Figure 5 Molecular weight distribution of Type 1 resin at the B stage, predicted through program RESRUN.FOR.

The molecular weight distribution is next extracted from the “reacted” molecules in the model. The M_n and M_w as a function of conversion are shown in Table II. The observed approximate molecular weight data (from size exclusion chromatography, SEC) are given. In this case, the trends in the data are similar, but the calculated M_n and M_w are somewhat different from the observed M_n and M_w . Two points may be noted: (1) the observed M_n and M_w are based on the SEC curve using polystyrene calibration. The SEC data are meaningful on a relative basis, but may not be accurate in the absolute sense; (2) the SEC data do not take unreacted MHCS into account when computing M_n and M_w , whereas the calculated M_n and M_w do include unreacted MHCS.

The calculated molecular weight distribution is next plotted in Figure 5. We can assign the peaks on the basis of molecular weight. Note that all species above molecular weight 1000 can be considered to be chain extended, i.e., molecules in which the cyclopentenyl double bond of DCPD also reacted.

Type 2 Resin

Experimentally, the same synthetic procedure is used to make Type 2 resin except that the two TCPD compounds (P and Q) are added together with DCPD (M). The same rate parameters are therefore used for this simulation. This calculation then serves two purposes: (1) it provides a test of the appropriateness of the rate parameters used in Type 1 resins, and (2) if a good fit is ob-

tained, this model indicates that the chemistry in both cases is the same.

The output of the program RESRUN.FOR for the Type 2 case is given in Figure 6. Again, the overall $[\text{MHCS}] = 1 \text{ mol/L}$, and mol fractions $D'_4 : D'_5 = 55.5 : 44.4$. The overall $[\text{DCPD}] + [\text{TCPD}] = 2.22 \text{ mol/L}$, and the mol fractions of the monomers $M : P : Q = 0.735 : 0.220 : 0.045$. The B-stage resin is obtained at roughly 50% conversion of DCPD olefins. In the reaction, the “semibatch” mode is used whereby the monomer mixture is added slowly to the MHCS solution.

The degrees of substitution on D'_4 and D'_5 are shown in the last two columns of Table I. The results are only slightly different from the Type 1 case. Note that the observed substitution pattern is not available for Type 2 resins because the SFC data are complicated and cannot be interpreted unambiguously. A plot of the calculated degree of substitution vs. conversion is given in Figure 7. The trends are also similar to the Type 1 resin (cf. Fig. 4).

The molecular weight distribution can be readily obtained from the model. The molecular weight plot (Fig. 8) shows a more complex distribution than the Type 1 resin case. The calculated M_n and M_w can also be compared with the approximate M_n and M_w observed by SEC (Table III). As in the case of Type 1 resin, the trends in the molecular weight data are similar, but the exact numerical values for the observed and the calculated M_n and M_w are different. (The SEC only provides approximate molecular weights; it is based on polystyrene calibration, and also does not include unreacted MHCS.)

Structure-Process Relationships

One purpose of computer simulation is to predict the effects of polymerization under different reaction conditions. In this way, we know the usefulness and the limitations of the computer techniques. Another purpose is to understand how molecular weight polydispersity depends on reactant stoichiometry, conversion, and DCPD reactivity. For simplicity, only Type 1 resins will be simulated.

Stoichiometry

For the purpose of illustration, we assume a homogeneous reaction where $k_1 : k_2 = 100 : 1$ (for DCPD). Also a conversion of 50% is assumed for

Parameters Used :

```

Fraction 4 member = 5.555556E-01
Si rings

K4 = 1.000000
z12 = 2.500000E-01      e12 = 4.500000E-01
z13 = 2.500000E-01      e13 = 4.500000E-01

K5 = 1.000000
z12 = 4.000000E-01      e12 = 4.500000E-01
z13 = 4.000000E-01      e13 = 4.500000E-01

k1 = 100.000000
k2 = 1.000000

[SiH rings] = 1.000000   [DCPD] = 2.222222

mol frac M = 7.350000E-01   mol frac P = 2.200000E-01
mol frac Q = 4.500000E-02

% CONVERSION = 53.511930

```

Results :

```

Functionality of Silicon Rings :
-----
          0      Mono      Di      Tri      Tetra      Penta      Func.
-----
4 Mem      .00     12.25     62.16     23.78     1.80     .00     2.15
5 Mem      .00      2.92     37.30     51.46     7.64     .67     2.66

Total      .00      8.11     51.11     36.08     4.40     .30     2.38

% M unreacted      =      1.35
% M mono subst.    =     94.55
% M di subst.      =      4.10

% P unreacted      =      .61
% P mono subst.    =     94.48
% P di subst.      =      4.91

% Q unreacted      =      2.00
% Q mono subst.    =      7.00
% Q di subst.      =     91.00

```

Mn = 727. Mw = 881. PD = 1.21

Figure 6 Output of the program RESRUN.FOR, for Type 2 resin at the B stage.

the B-stage resin. Let s = molar ratio of MHCS/DCPD. For s varying from 0.90 to 1.10, the molecular weight can be readily simulated using the program RESRUN.FOR. The result is given in Table IV. It appears that the effect of stoichiometry on molecular weight polydispersity is comparable; thus, a 10% change in stoichiometry causes a 10% change in polydispersity.

Conversion

We next examine the effect of conversion, assuming again that $k_1 : k_2 = 100 : 1$ and stoichiometry

$s = 1.0$. For conversions less than 50%, the molecular weight polydispersity is close to 1.1 (Table V). Above 50%, the polydispersity rises rather rapidly.

Cyclopentene Reactivity

In the previous two cases $k_1 : k_2 = 100 : 1$. This ratio may change as a result of temperature fluctuations or trace catalyst activation. To assess this effect, k_1/k_2 is allowed to vary from 1 : 100 to

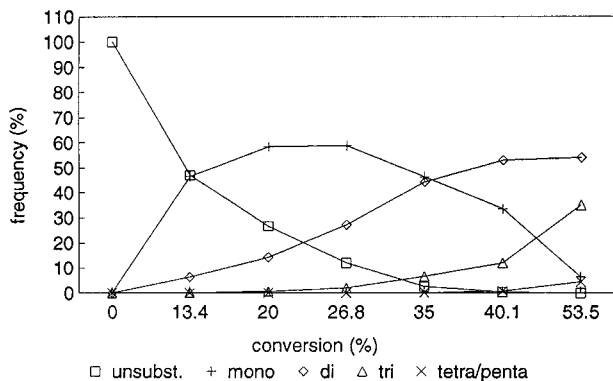


Figure 7 Substitution pattern of DCPD on the MHCS rings as a function of conversion for Type 2 resin, simulated through program RESRUN.FOR.

20 : 100. The conversion is kept at 50% and $s = 1.0$. The result is shown in Table VI.

Conversion and Stoichiometry

It is of interest to see how the combined effects of conversion and stoichiometry have on molecular weight. The result is shown in Figure 9. At 50 to 52% conversion, the effect of stoichiometry and conversion is relatively small. However, at higher conversion, stoichiometry and conversion together can produce rather large molecular weight polydispersity.

Sample Heterogeneity

Thus far in computer modeling, we have assumed homogeneous reactions. In a hypothetical case, we

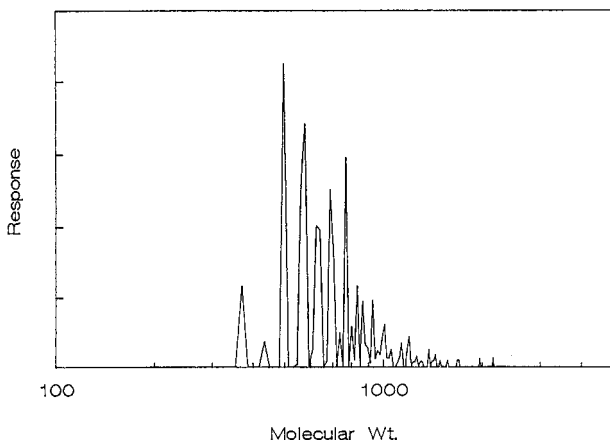


Figure 8 Molecular weight distribution of Type 2 resin at the B stage, predicted by program RESRUN.FOR.

Table III Observed and Calculated Molecular Weights for the Type 2 Resin

Observed ^a			Calculated		
Conversion (%)	M_n	M_w	Conversion (%)	M_n	M_w
12.5	497	589	13.4	445	463
25	526	660	25	478	511
37.5	561	735	37.5	559	630
50	616	845	50	731	911

^a Determined by size exclusion chromatography, based on polystyrene standards. Values are approximate and are to be used on the relative basis only.

can visualize a reaction possessing sample heterogeneity due to the polymerization process. Possible sources are local hot spots, inadequate agitation, adventitious catalyst activation, and diffusion-controlled reactions. A hypothetical calculation can be made assuming 5% (by weight) of high molecular weight portion and 95% of low molecular weight portion (with assumed molecular weight = 500).

	Proportion	Case A	Case B
Assumed:	95%	$M = 500$	$M = 500$
	5%	$M = 1300$	$M = 3000$
Average mol. wt.:		$M_n = 540$	$M_n = 625$
		$M_w = 600$	$M_w = 1100$
		$M_w/M_n = 1.1$	$M_w/M_n = 1.76$

Thus, even a small amount (5%) of high molecular weight species can have a large impact on the molecular weight polydispersity.

Table IV Statistical Simulation^a (Program RESRUN.FOR) of Molecular Weight as a Function of Stoichiometry ($s = \text{MHCS/DCPD}$) for Type 1 Resin

s	M_n	M_w	M_w/M_n	Conv. (%)
0.90	737	976	1.32	49.5
0.95	692	864	1.25	49.7
1.00 ^b	662	809	1.21	50.0
1.05	652	775	1.19	49.3
1.10	628	720	1.15	50.4

^a Simulation was done for 2000 MHCS rings using $k_1 : k_2 = 100 : 1$; addition rate (B side to A side) = 0.5% per increment.

^b Results are the averages of two runs.

Table V Effect of Conversion on Molecular Weight (Simulation through Program RESRUN.FOR)^a for Type 1 Resin

Conversion	M_n	M_w	M_w/M_n
39.8	530	577	1.09
45.5	588	665	1.13
50.0	662	809	1.22
52.31	724	927	1.28
54.6	800	1083	1.35
55.71	850	1260	1.48
57.98	962	1567	1.63
60.3	1141	2299	2.01

^a Simulation carried out on 2000 MHCS rings with $k_1 : k_2 = 100 : 1$, $s = 1.0$, addition rate (B to A) = 0.5% per increment.

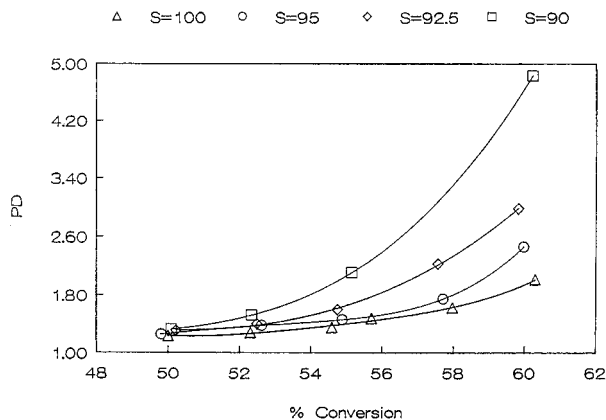
Uses and Limitations of the Statistical Model

The statistical model developed in the above sections provided rather good agreement with experimental data. The model can be used in the following way: (1) permit analytical data on silicone-carbon resin to be interrelated. (2) Permit possible detection of deviant data. (3) Provide a feel as to the sensitivity of data to perturbations. (4) Assist in setting specifications on products. (5) Provide a better understanding of the reaction mechanism. (6) Permit predictions to be made of polymer structure and molecular weight on samples made under different stoichiometries and reaction conditions. Another possibility is to learn about catalyst differences; e.g., different catalysts may have different reactivities towards norbornene and cyclopentene double bonds.

Two limitations of the model need to be recognized: (1) this is a statistical model. All the rate parameters are relative to each other and are not absolute values. (2) Similarly, the concentrations of various species are relative to one another.

Table VI Effect of k_1/k_2 on Molecular Weight (Simulation through Program RESRUN.FOR) for Type 1 Resin

$k_2 : k_1$	M_n	M_w	M_w/M_n
1 : 100	662	809	1.22
5 : 100	830	1196	1.44
10 : 100	985	1625	1.65
20 : 100	1179	2259	1.92

**Figure 9** Molecular weight polydispersity as a function of both conversion and stoichiometry ($s = \text{MHCS}/\text{DCPD}$) for Type 1 resin.

Comparison of Statistical vs. Kinetic Approaches

In a separate work, a kinetic approach²¹ had been devised for Type 1 resins. Owing to mathematical complexity, the kinetic approach has not been formulated for Type 2 resins. In contrast, the statistical approach as described here can be used for both types of resins.

A comparison can be made between the statistical and the kinetic approaches (Table VII). The kinetic approach gives the exact solution of the kinetic equations. The solution of the kinetic equations gives the time dependence of the concentrations of the various species. The rate constants used are absolute values. The TKSolver software²² permits flexibility in changing the mode of reaction. Thus, reverse addition and simultaneous addition of the reactants are possible with a minimum amount of changes. The major disadvantage of the kinetic approach is that the concentrations of only the substituted MHCS and the reacted DCPD are explicitly included in the kinetic equations. The formation of polymers is simulated indirectly with either an approximation process or the Miller-Macosko method.²³ The M_w obtained thus may not be accurate in the semibatch case. Also, molecular weight distributions cannot be generated in the kinetic case.

In comparison, the statistical approach does not have the last limitation described above. It simulates the polymerization process and obtains an ensemble of molecules from which the actual molecular weight distribution can be obtained. However, owing to the nature of the Monte Carlo

Table VII Comparison of Information Contents of Statistical and Kinetic Approaches

Statistical Approach (Program RESRUN.FOR)	Kinetic Approach (Program RESGO.TK) ²¹
(1) individual substitution patterns of D'_4 and D'_5	(1) <i>average</i> substitution patterns (on $D'_4 + D'_5$)
(2) molecular weight distribution, M_n , M_w , and polydispersity	(2) estimates of molecular weight averages; molecular weight distribution unavailable
(3) concentration vs. <i>conversion</i> of various substituted MHCS species	(3) concentration vs. <i>time</i> of various substituted MHCS species
(4) concentration vs. <i>conversion</i> of unreacted, monoreacted, and directed DCPD	(4) concentration vs. <i>time</i> for various DCPD species
(5) no information on time dependence (of conversion)	(5) conversion vs. time is available
(6) applicable to both Type 1 and Type 2 resins	(6) applicable presently to Type 1 resin only

simulation, the rate constants are relative numbers. As a result, we get the concentration of various species only as a function of conversion but not of time.

EXPERIMENTAL SECTION

Computer simulation was carried out on an IBM 486/50 personal computer. Program RESRUN.FOR was written in Microsoft Fortran. The program is self-contained with no external subroutine necessary. Plots were made using SlideWrite.²⁴

Molecular weights were determined using size exclusion chromatography (SEC) using polystyrene standards. Conversion was determined from ¹H-NMR (for unreacted DCPD olefins), and through quantification of silyl hydride with a mercuric chloride procedure. Substitution patterns on the MHCS rings were determined through supercritical fluid chromatography (SFC) and ²⁹Si NMR.

CONCLUSION

In this work, a computer approach has been described to simulate the reaction processes leading to the formation of silicone-carbon resins. A computer program (RESRUN.FOR) have been tested using inputs that correspond to different reaction conditions. Refinements have been made, and the program now runs smoothly for reaction condi-

tions being considered. A number of simulations have been carried out showing satisfactory fit with the observed data.

One use of the statistical model is to gauge the sensitivity of molecular weight polydispersity of the resins to different experimental parameters. The simulation result suggests that polydispersity is sensitive to conversion, reactant stoichiometry, and to the relative reactivity of norbornene/cyclopentene double bonds in dicyclopentadiene.

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REFERENCES

1. P. J. Cowan, U.S. Pat. 4,877,820 (October 31, 1989).
2. R. T. Leibfried, U.S. Pat. 4,900,779 (February 13, 1990).
3. R. T. Leibfried, U.S. Pat. 4,902,731 (February 20, 1990).
4. J. K. Bard and J. S. Burnier, U.S. Pat. 5,068,703 (November 26, 1991).
5. P. E. Barnum and R. L. Brady, U.S. Pat. 5,242,979 (September 7, 1993).

6. P. E. Barnum and R. L. Brady, U.S. Pat. 5,171,817 (December 15, 1992).
7. R. T. Leibfried, U.S. Pat. 5,013,809 (May 7, 1991).
8. R. T. Leibfried, U.S. Pat. 5,077,134 (December 31, 1991).
9. R. T. Leibfried, U.S. Pat. 5,124,423 (July 5, 1990).
10. R. T. Leibfried, U.S. Pat. 5,124,375 (June 23, 1992).
11. R. T. Leibfried, U.S. Pat. 5,196,498 (March 23, 1993).
12. B. Marciniec, Ed., *Comprehensive Handbook on Hydrosilation*, Pergamon Press, London, 1992, and references therein.
13. Y. Chujo and J. E. McGrath, *J. Macromol. Sci.-Pure Appl. Chem.*, **A32**, 29 (1995).
14. G. G. Lowry, Ed., *Markov Chains and Monte Carlo Calculations In Polymer Science*, Marcel Dekker, New York, 1970.
15. H. J. Harwood, Y. Kodaira, and D. L. Newman, *Comput. Chem. Instrum.*, **6**, 57 (1977).
16. T. A. Duever, K. F. O'Driscoll, and P. M. Reilly, *ACS Symp. Ser.*, **404**, 282 (1989), and references therein.
17. H. N. Cheng and M. A. Bennett, *Anal. Chem.*, **56**, 2320 (1984), and references therein.
18. J. Lu, H. Zhang, and Y. Yang, *Makromol. Chem., Theory Simul.*, **2**, 747 (1993).
19. J. Somvarsky and K. Dusek, *Polym. Bull.*, **33**, 377 (1994).
20. S. Dutton, H. Rolfes, and R. F. T. Stepto, *Polymer*, **35**, 4521 (1994).
21. L. J. Kasehagen, H. N. Cheng, and P. J. Cowan, *Angew. Makromol. Chem.*, to appear.
22. *TKSolverTM, Release 2.0—Introduction Manual*, Universal Technical Systems, Inc., Rockford, IL.
23. C. W. Macosko and D. R. Miller, *Macromolecules*, **9**, 199 (1976).
24. *SlideWrite PlusTM—The Presentation Graphics Solution*, Advanced Graphics Software, Inc., Sunnyvale, CA.