Polymer Bulletin 18, 463–471 (1987)

Polymer Bulletin

The hydrosilylation cure of polyisobutene

C.W. Macosko[1] **and J.C. Saam**[2]

[1] Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA

[2] Dow Corning Corporation, Midland, MI 48686, USA

SUMMARY

A liquid polyisobutene oligomer with unsaturated chain ends undergoes hydrosilylation with $HMe_2SiOMe_2SiOMe_2SiH$ or $Si(OMe_2SiH)_4$ to give higher molecular weight polymers or elastomers. A major side reaction consumes SiH to give redistributed siloxane in the resulting polymers and gaseous silanes and siloxanes as by-products. A second side reaction results in loss of reactivity in the oligomer due to a shift of the terminal double bond to an internal position. If the side reactions are taken into account, it is possible to forecast quantitatively molecular weight, gel point and modulus from the conversions of $>SiH$, $>C=CH_2$ and the chain entanglement concentration reported for polyisobutene in the literature.

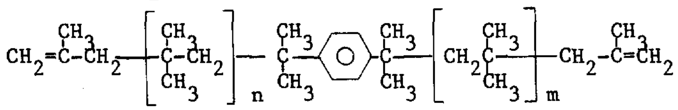
INTRODUCTION

Hydrosilylation (reaction 1) has been used extensively in cross linking studies of elastomer networks because of its presumed straight forward nature and freedom from side reactions.

$$(1)\quad >SiH + -CH=CH_2 \longrightarrow\ >SiCHCH_2-$$

For example, hydrosilylation was employed for end linking polydimethylsiloxane networks to verify a statistical method of describing elastomer network structures and how they related to macroscopic properties where the required empirical information was the degree of conversion of the reactive groups (1). Subsequent work on the same system revealed, however, an extraneous side reaction which consumed $>SiH$ without forming end links (2). The side reaction was originally presumed to be a platinum-catalyzed reaction of the silane with moisture in the reagents to produce silanol.

The present investigation extends these studies by applying hydrosilylation to end-linking a terminally unsaturated liquid polyisobutene (B_2) described by Kennedy and coworkers (3).



$$CH_2=C(CH_3)-CH_2-\left[C(CH_3)_2-CH_2\right]_n-C(CH_3)_2-C_6H_4-C(CH_3)_2-\left[CH_2C(CH_3)_2\right]_m-CH_2-C(CH_3)=CH_2$$

(B_2)

This material, because of its hydrocarbon character, can be easily maintained in a dry state and interactions of SiH with moisture during end-linking will be minimized. Further, any new siloxane structures formed during end-linking can be readily detected by NMR. Bifunctional (A_2) or tetrafunctional (A_4) endlinkers are used with a dry catalyst, cis-$[(C_2H_5)_2S]_2PtCl_2$ dissolved in toluene solutions.

A_2: $HMe_2SiOMe_2SiOSiMe_2H$ A_4: $Si(OSiMe_2H)_4$

The aim of this work is to demonstrate an alternative to the sulfur cure for unsaturated polyisobutene as well as to show how the recursive method of statistically calculating molecular parameters in stepwise polymerization or cross-linking can be applied to yet another polymer system (4). Further light will also be shed on side reactions occurring during end linking via hydrosilylation.

EXPERIMENTAL

Siloxanes A_2 and A_4 were obtained from Petrarch Chemicals and B_2, $\bar{M}_n$=1400, was obtained from Prof. J. P. Kennedy, Univ. of Akron, Akron, OH. The catalyst was used as a 0.1% stock solution in toluene. Rheological measurements during end-linking were made with a Rheometrics System IV Mechanical Spectrometer. NMR data were obtained with the Nicolet 293A 300 MHz spectrometer. FTIR spectra were obtained on a Nicolet 60SX using 64 scans.

Previously dried B_2 that was devolitalized and contained 2.7×10^{-5}g of catalyst/g. of B_2 was mixed at room temperature with enough A_2 to obtain the desired initial ratio (r) of ⋗SiH to >C=CH_2. Excessive amounts of gas often formed during end linking with A_4 and it was necessary first to conduct part of the end-linking experiment with a large excess of A_4. This was then diluted with more B_2 to give the appropriate value of r and the process was continued in the fixture of the rheometer. In this fashion foaming and bubbles were minimized. Results from some runs are shown in Figures 1 and 2. The process was considered complete when viscosity, η, or storage modulus, G', achieved a constant value. It was presumed that G' at ω=10 rad $sec.^{-1}$ and at 5% peak strain was an equilibrium value under these conditions since little or no change was seen when ω was varied from 10^2 to 10^{-1} rad $sec.^{-1}$ at the end of a run.

Conversions of ⋗SiH,P_A, and >C=CH_2, P_B, were determined from the ^{1}HNMR spectrum obtained in CCl_4 solutions of polymers made from A_2. The area of the signals (SiH at 4.70 ppm and >C=CH_2 at 4.80 and 4.63 ppm, relative to $SiMe_4$) were referenced to the aromatic peak in B_2 (6.95-7.05 ppm) which remained unchanged during the process. A similar technique could be applied to gels made from A_4 when the end-linking process was terminated near the gel point. The resulting gels were swollen in CCl_4 containing about 1%S to prevent further reaction. It was necessary, however, to degrade the more highly cured elastomers made from A_4 to render them soluble in CCl_4 and amenable to quantitative analysis by ^{1}HNMR. The siloxane cross links were cleaved by first swelling the elastomers in CCl_4 and then equilibrating with $(Me_3Si)_2O$ and CF_3SO_3H catalyst at room temperature. An identical procedure with previously characterized soluble polymers made from A_2 and B_2 established that these conditions did not alter the content of SiH but caused some shift of residual >C=CH_2 to an internal position of B_2.

Data on chemical shifts in the $SiCH_3$ region were obtained with the model compounds given in Table I. The series $RMe_2SiO(Me_2SiO)_nMe_2SiR$ (where R=$CH_3CH_2CH_3CHCH_2$, n=0,1,2,3,4) was obtained by hydrosilylation with excess

Figure 1. Plots of viscosity, η, vs. polymerization time where r=1.0 for the hydrosilylation of B_2 with A_2 at 85°C and of B_2 and A_4 at 51°C.

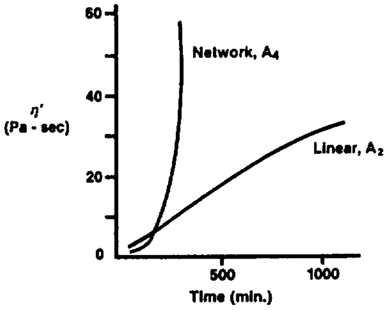
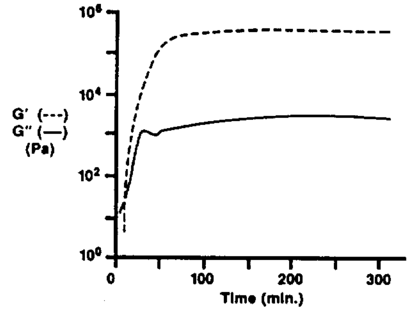


Figure 2. Dynamic shear moduli vs. time for the cure of B_2 with A_4 at 85°C, r=1.0. Measurements at 5% strain at ω=10 rad $sec.^{-1}$.



$CH_3CH_2(CH_3)C{=}CH_2$ of $HMe_2SiO(Me_2SiO)_nMe_2SiH$. The latter intermediates were >98% pure by GC. Products of the hydrosilylation were purified by distillation and structures were confirmed by both ^{1}HNMR and ^{29}SiNMR spectroscopy.

Table I

Chemical Shift Data for $RMe_2SiO(Me_2SiO)_nMe_2SiR$ where $R{=}CH_2(CH_3)CHCH_2CH_3$

Structure	n	Chemical Shift of $Si\underline{CH_3}$ in the ^{1}HNMR[a)] p.p.m. at 200.1 MHz at position[b)] 1	2	3	Chemical Shift in the ^{29}SiNMR[a)] p.p.m. at 39.75 MHz at position[b)] 1	2	3
I	0	0.051	-	-	6.73	-	-
II	1	0.072	-0.003	-	6.97	-21.84	-
III	2	0.082	0.036	-	7.07	-22.23	-
IV	3	0.074	0.033	0.053	7.15	-21.93	-22.51
V	4	0.073	0.033	0.057	7.16	-21.89	-22.26

a) In CCl_4 relative to $SiMe_4$. b) Silicon atoms are numbered from the terminal position attached to the R group, $R\underset{1}{Me_2}SiO(\underset{2}{Me_2}SiO)_n\underset{\text{etc.}}{}\underset{1}{Me_2Si}R$.

RESULTS

Clear polymers soluble in common solvents formed from A_2 and B_2. Number average molecular weights ranged up to M_n=50,000 and weight average to M_w=90,000 depending on r. Insoluble dry elastomers or tacky gels, depending the extent of reaction, formed from A_4. The ^{1}HNMR spectra of the polymers and gels resembled those of B_2 (3) with greatly diminished intensities for $>C=CH_2$ and new signals for $OSi(C\underline{H}_3)_2$. Figure 3 shows that the signal for $OSi(C\underline{H}_3)_2H$ (0.17 ppm) from A_2 in the original mixture disappeared. A strong new signal, A, corresponding to $R'(C\underline{H}_3)_2SiO$ (0.095 to 0.085 ppm) appeared. Signal, C, at -0.009 ppm was assigned to the central $(C\underline{H}_3)_2SiO$ unit in the corresponding structure II, Table I, which was anticipated from reaction 1. However, a strong spurious signal, B, for $SiC\underline{H}_3$ also appeared at 0.028 ppm and was assigned to $(C\underline{H}_3)_2SiO$ at position 2 in the corresponding structure III, Table I. The example in Figure 3 was run in high vacuum to eliminate the possibility of reaction of SiH with oxygen or moisture in the air. Identical chemical shift patterns, however, were obtained on samples run in air.

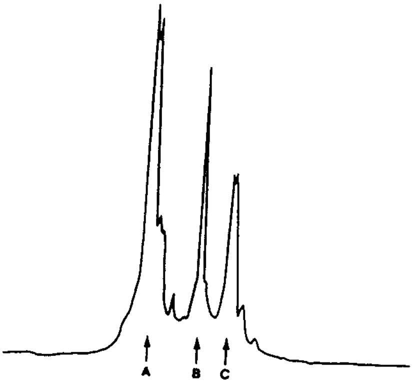


Figure 3. ^{1}HNMR spectrum of in the $SiC\underline{H}_3$ region of the polymer obtained from the polymerization A_2 with B_2 (r = 1.0) in high vacuum (10^{-6} torr) using out-gassed reactants. Peak assignments based on data given in Table I. Peak A (0.094 ppm, relative area 1.00) was assigned the structure $R'(C\underline{H}_3)_2SiO-$. Peak B (0.028 ppm, area 0.30) was assigned the structure $-O[(C\underline{H}_3)_2SiO]_2$. C (-0.009 ppm area 0.36) was was assigned the structure $(C\underline{H}_3)_2SiO$. Peak B was not anticipated from reaction 1.

The ^{29}SiNMR spectra of the same polymer gave major signals at 6.39ppm for $R'Me_2SiO$ and at -21.99ppm for Me_2SiO both of which were anticipated for structure II. Again a spurious separate signal was detected close to the peak corresponding to $R'Me_2SiO$ at 6.47 ppm. The later was also attributed to the presence of a higher siloxane homolog based on the chemical shift trends in Table I. The ^{29}SiNMR showed no signals in the region of -11 to -12 ppm which might be attributed to Me_2SiOH. This was further confirmed by the absence of any bands for $>SiOH$ in the region 3150 to 3600 cm^{-1} in the FTIR spectra in either the above polymer or in polymers made by polymerization of B_2 with A_2 in air.

Therefore, although end-linking proceeded via reaction 1, a second process was occurring which, from the relative area intensities in the NMR spectra, gave about 20 to 30% (based on end linker) of a structure similar to III in Table I. This was proposed to form via the disproportionation reactions 2 and 3.

$$(2)\quad 2R'Me_2SiOMe_2SiOMe_2SiH \xrightarrow{Pt} R'Me_2SiO(Me_2SiO)_2Me_2SiR' + (HMe_2Si)_2O$$

and

$$(3)\quad (n+1)(HMe_2Si)_2O \xrightarrow{Pt} HMe_2SiO(Me_2SiO)_nMe_2SiH + n\ Me_2SiH_2$$

(R'= H or the polymeric residue from B_2; n = 1 or 2)

The two processes, separately or in combination, amount to formation of new endlinker and simultaneous loss of SiH since by-produced disiloxane (reaction 2) or silane (reaction 3) are well over their boiling points and readily lost from the system under the present conditions. Similar processes are proposed when B_2 is cross-linked with A_4. Siloxane - $SiCH_3$ bond redistribution under conditions of hydrosilylation have been reported by Speier and Stober (5) and siloxane - SiH bond redistribution by Andrianov and coworkers (6). More recently Curtis and coworkers have shown that such processes were ubiquitous and readily took place with a variety of siloxanes bearing $-OMe_2SiH$. Complexes of Ir, Rh, Pt and Pd were catalysts for the process with varying degrees of effectiveness (7). The present system proved to be no exception.

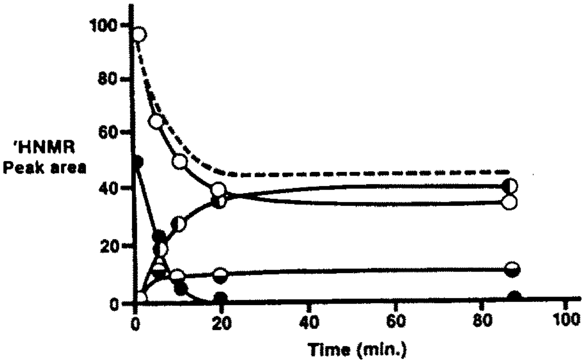


Figure 4: Peak areas relative to the aromatic peak in B_2 in the ^{1}HNMR vs. time during reaction at 80°C of with A_2 (r = 1.89). -○-: $Si\underline{H}$,-●-: $C=C\underline{H}_2/2$,-◐-: $R'Si(C\underline{H}_3)_2/6$, corresponding to peak A, Fig. 3; -◒-: $[(C\underline{H}_3)_2SiO]_2/12$ corresponding to peak B, Figure 3; ---anticipated disappearance of SiH based on $>C=CH_2$

Reactions 2 and 3 are considered to occur simultaneously with hydrosilylation, reaction 1. Figure 4 traces the disappearance of >SiH, $>C=CH_2$ and the formation of products during polymerization of B_2 with an excess of A_2. This shows that more >SiH is consumed than anticipated from reaction 1 and that the discrepancy developed while the adduct, $RSi(CH_3)_2O-$, formed. Structure III formed only during generation of adduct and its final amount compensated for the discrepancy between the observed consumption of >SiH and that expected from simple hydrosilylation.

The consumption of $>C=CH_2$ in B_2 paralleled the appearance of product and there was no extraneous loss of this functionality. In other runs taken to the gel point with A_4, however, about 15% of the terminal double bond in B_2 shifted to an internal position as evidenced by the appearance of a signal at 5.10 ppm in the ^{1}HNMR. Similar rearrangements in structurally analogous low molecular weight olefins have been documented elsewhere when H_2PtCl_6 was the catalyst (8). Also, a single example of curing B_2 with A_4 with H_2PtCl_6 was documented but no evidence was given for the above shift of double bond or the reactions 2 and 3 (9).

Molecular weight averages in polymerization with A_2 and G' in cross-linking with A_4 reached maximum values as the initial ratio of >SiH to $>C=CH_2$ (r) was varied (Figures 5 and 6). However, the maxima at r=1.2 for A_2 and 1.3 for A_4 deviated significantly from the anticipated value of r=1 in an end-linking process based on reaction 1. The discrepancies can only be explained in terms of the side reactions 2 and 3 which lead to loss of >SiH and occur either prior to or during network formation.

Figure 5:
Effect of r on number average, M_n, and weight average, M_w, molecular weight for the polymerization of B_2 and A_2 at 85°C.

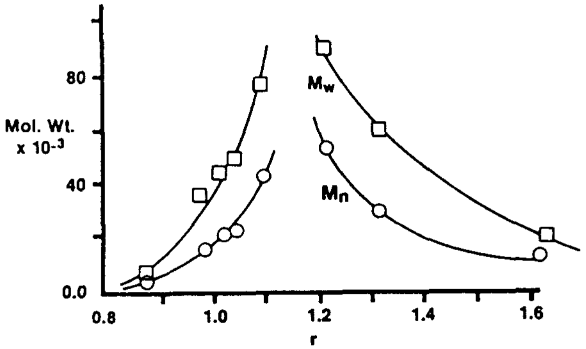
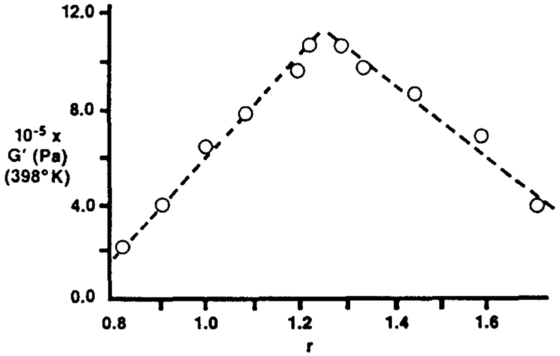


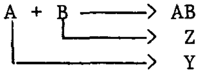
Figure 6:
Effect of r on the final storage modulus in cures of B_2 with A_4 at 125°C.



Discussion

Simultaneous occurrence of side reactions 2 and 3 during hydrosilylation results in loss of SiH without forming end links to change the value of r via volatilization of the by produced silanes. The value of r can also be altered by loss of the terminal double bond to an unreactive internal position in the polymer by a second side reaction. The net effect of both side reactions will be a lower than anticipated molecular weight with A_2 or modulus with A_4. A schematic representation of the over-all process can then be given by

(4)



Where A represents SiH, B >C=CH$_2$, AB represents endlinks formed by hydrosilylation with A_2, A_4 or the non-volatile species formed in reactions 2 or 3, Y represents an equivalent of SiH lost as a gaseous silane in reaction 2 or 3 and Z represents an unreactive double bond in B_2 found at 5.10 ppm in the ^{1}HNMR. If A_o and B_o are the initial amounts of A and B respectively, r = A_o/B_o and r' is the effective ratio of A to B in forming end links, the observed conversions in this scheme will be given by

(5)

$$P_a \equiv \frac{A_o - A}{A_o} = \frac{AB+Y}{A_o} \qquad P_y \equiv Y/A_o$$

$$P_b \equiv \frac{B_o - B}{B_o} = \frac{AB+Z}{B_o} \qquad P_z \equiv Z/B_o$$

and the effective conversions of $>SiH$, P'_a, or of $>C=CH_2$, P'_b, to endlinks will be given by

$$(6)\qquad P'_a \equiv \frac{AB}{A_o-Y} = \frac{P_a-P_y}{1-P_y} = \frac{P_b-P_z}{r(1-P_a)+(P_b-P_z)}$$

$$P'_b \equiv \frac{AB}{B_o-Z} = \frac{P_b-P_z}{1-P_z} = \frac{r(P_a-P_y)}{1-P_b + r(P_a-P_y)}$$

$$r' \equiv \frac{A_o-Y}{B_o-Z} = r\,\frac{1-P_y}{1-P_z} = P'_b/P'_a$$

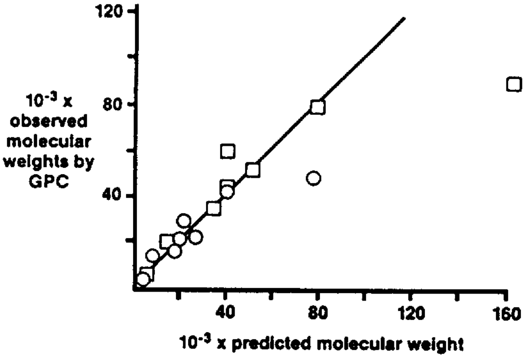
Thus, knowing either P_y or P_z, the effective conversions to end links can be calculated from the observed conversions.

Number and weight average molecular weights were predicted for the runs with A_2 using the expressions below and the effective conversions described in equation 6.

$$(7)\qquad Mn = \frac{r'M_A + M_B}{r'(1+r')} \qquad\qquad (8)\qquad Mw = \frac{r'(1+r')M_A^2+1/2(3+r')M_B^2+4M_AM_B}{(r'M_A+M_B)(1+r')}$$

Where M_A and M_B are the number average molecular weights of A_2 and B_2 respectively. Equations 7 and 8 are special cases of the general equations for M_n and M_w given in reference 4 where either P'_a or P'_b are unity (the case in runs with A_2) and where $M_w/M_n=1.5$ for B_2. Little loss of $>C=CH_2$ to rearrangement was seen in polymerization with A_2, hence $P_z=0$. Good agreement between observed and predicted molecular weights was seen, Figure 7, with one exception at the highest molecular weight and conversion.

Figure 7: Observed vs. predicted molecular weights in reactions of A_2 and B_2. ○:M_n □:M_w. Solid line indicates perfect agreement with theory.



The scheme in reaction 4 is therefore presumed to represent the process within the present limits of accuracy. It is also presumed that an analogous process occurs in cures with A_4. This was illustrated in runs with A_4 taken to the gel point and then quenched by cooling. The gels could be analyzed by ^{1}HNMR for A, B and Z when they were swollen in CCl_4 which contained 0.5 to 1% sulfur to suppress further reaction. The observed conversions and those defined by equation 6 could then be compared in the expression for critical conversions at the gel point.

$$(9) \qquad P'_aP'_{b\,\mathrm{gel}} = \frac{1}{(f_a-1)\ (f_b-1)}$$

Where f_a is the weighted average functionality of end-linker and f_b that of B_2 (4).

Table II

Conversions at the Gel Point for the Reaction of A_4 and B_2 (r=1)

t°C	P_a	P_b	P_z	P_aP_b	P'_a	P'_b	$P'_aP'_b$
65	0.70	0.55	--	0.38	0.65	0.55	0.36
80	0.73	0.58	0.18	0.42	0.60	0.49	0.29
95	0.79	0.55	0.17	0.43	0.65	0.46	0.30
110	0.76	0.59	0.17	0.45	0.64	0.51	0.32
(Predicted)[a]	0.58	0.58	--	0.33	--	--	--
(Predicted)[b]	0.73	0.60	--	0.44	0.62	0.52	0.32

[a] Assume equation 10 and no side reactions $f_a = 4.0$ and $f_b = 2.0$. [b] Assume equation 10 and side reactions in scheme so 4 $P_z = 0.17$ and $P_y = 0.30$ $f_a = 4.0$ and $f_b = 2.0$.

Table II shows that the critical conversions at the gel point with A_4 are in agreement with theory when the sequence in scheme 4 is presumed and conversions are defined by equation 6. The data also suggests that the side reactions tended to occur to a lesser extent at lower temperatures. Based on sample calculations the experiment was insensitive to any changes in functionality that might have occurred .

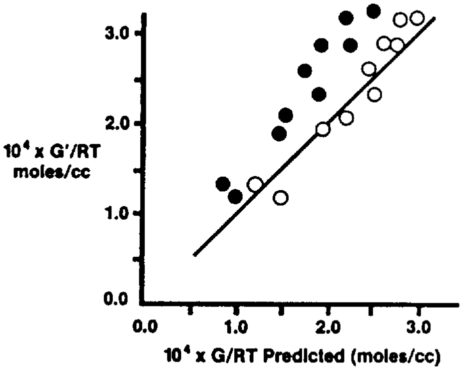
The equation for ideal elastic behavior can be expressed as equations 10 or 11, depending on the importance of topological chain entanglements. These can then be compared in predicting of equilibrium shear modulus, G, in the fully cured elastomers.

$$(10) \quad G/RT = g[A_4]_oP(X_F) \quad \text{or} \quad (11) \quad G/RT = g[A_4]_oP(X_F) + G^o_N/RT(T_E)$$

Where g is a constant converting concentrations of cross links to effective concentrations of network chains and g = 1 for A_4; $[A_4]_o$ the initial concentration of A_4; $P(X_F)$ the probability that a cross link is connected to the network; G^o_N/RT the entanglement concentration of uncured PIB based on the measured plateau modulus (10), and T_E the probability that an entanglement is connected to the network.

The probabilities $P(X_F)$ and T_E were estimated by the recursive statistical method for stepwise polymerization which requires only knowledge of conversions of the reactive groups (4). In the present case the conversions P'_a and P'_b were obtained from ^{1}HNMR measurements on elastomers which had been solubilized by the procedure described in the experimental section. It was not possible to estimate P_z directly by this procedure but it was assumed to be the same as that seen in the runs with A_4 terminated at the gel point. It was also approximated that the weighted average functionality of A_4 was effectively 4 regardless of the side reactions (see note b, Table II). The results of these calculations are shown in Figure 8. Best agreement is seen when equation 12 which includes the effect of entanglements is used to compute G/RT.

Figure 8:
Predicted G/RT at 125°C Vs. that obtained from modulus measurements in cures of B_2 with A_4. Solid line indicates perfect agreement with theory. ●: Based on equation 11 where entanglements are not taken into account. ○: Based on equation 12 where entanglements are included.



ACKNOWLEDGEMENT

The authors wish to acknowledge the Dow Corning Corporation for granting J. Saam leave so he could conduct the major part of this work at the Department of Chemical Engineering and Materials Science, University of Minnesota.

REFERENCES

1). a) E. M. Valles and C. W. Macosko, Macromolecules, 12, 521 (1979) and 12, 673 (1979).
b) M. Gottlieb, C.W. Macosko, G.S. Benjamin, K.D. Meyers and E. W. Merrill, Macromolecules, 14, 1039 (1981) and leading references therein.
2. C. W. Macosko and G. S. Benjamin, Pure and Appl, Chem. 1505 (1981).
3. J. P. Kennedy, V.S.C. Chang, R. A. Smith and B. Ivan, Polymer Bulletin 1, 575 (1979).
4. D. R. Miller, E. M. Valles, and C. W. Macosko, Polym. Eng. and Sci., 19(4), 272, (1979) and leading references therein.
5. M. R. Stober, M.C. Musolf, and J. L. Speier, J. Org. Chem. 30, 1651 (1965).
6. K. A. Andrianov, B. G. Zavin, G. F. Sablina, L. A. Leites, B. D. Lavrukhin and A. M. Endokomov, Výsokomol. Soedin., Ser. B16(5), 330 (1974).
7. W. A. Gustavson, P. S. Epstein and M. D. Curtis, J. Organometall. Chem. 238, 87 (1982).
8. J. Saam and J. Speier, J. Am. Chem. Soc. 83, 1351 (1961).
9. P. H. Sung, S. J. Pan, J.E. Mark, J. E. Lackey, and J. P. Kennedy, Polymer Bulletin 9, 375 (1983).
10. J. W. Ferry "Viscoelastic Properties of Elastomers" John Wiley and Sons, Inc., N.Y. (1980), p. 606.

Accepted September 24, 1987 K