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Structure and Viscosity of Poly(dimethylsiloxanes) with Random Branches

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ABSTRACT: Viscosity rise and extent of reaction were followed during the stepwise polymerization of vinyl-terminated poly(dimethylsiloxane) with tri- and tetrafunctional hydrosilanes. Gel point results and M_w data by light scattering agree with predictions from branching theory. This indicates that the influence of side reactions, substitution effects, and ring formation is small. The bulk viscosity of the branched molecules was found to correlate with the weight average molecular weight of the longest linear chain through the molecules, $M_{L,w}$, and with gM_w, where g is the ratio of branched to linear polymer radii of gyration.

A major area of study of the physics of polymer science is the one concerned with the relations between measurable viscoelastic properties and molecular parameters. One of the best known relations in this area is the one that correlates the zero shear rate viscosity of polymer melts to their average molecular weight. If the polymer is linear,

$$\eta_0 = KM_w^a \qquad (1)$$

with $a = 3.4$ for $M_w > M_c$ and $2.5 \geq a \geq 1.0$ for $M_w < M_c$, where K is a temperature-dependent constant, η_0 is the zero shear rate viscosity, M_w is the weight average molecular weight, and M_c is the critical molecular weight beyond which the influence of entanglements begins to be important. Equation 1 applies to all common polymers, both in bulk and in concentrated solution.[1]

For branched systems the relation between η_0 and the molecular parameters is not so well established. The introduction of a few long branches seems to decrease the viscosity of the polymer if it is compared with the linear polymer of the same molecular weight.[2-7] However, when the branches are long enough to form many entanglements, the viscosity of the branched system is higher than that of the linear polymer of the same molecular weight.[8-11]

Graessley[11] has recently reviewed the effect of long branches on η_0 for model branched materials, four- and six-arm star molecules. He finds a good correlation for the viscosity data with

$$\eta_0 = K(gM_w)^a \qquad (2)$$

where $a \simeq 3.4$, the same as for the linear case, and g is the ratio of the squares of the radii of gyration of a branched to the linear chain of the same M_w, s_b^2/s_l^2. Thus $g \leq 1$ and decreases with increased branching. Graessley finds that eq 2 holds up to $gM_w \simeq 2 \times 10^5$. At higher gM_w values, presumably when the branches entangle, η_0 rises even more steeply for these branched polymers as has been observed in other systems.[8-10]

Randomly branched molecules, rather than regular stars, are the type which occur in most commercial polymerizations. However, their structure, and thus g, is difficult to determine. By step-reaction polymerization a randomly branched system of known structure can be obtained using a polyfunctional comonomer. In this work we have studied the viscosity rise during polymerization of a well-defined system composed of long molecules of bifunctional poly(dimethylsiloxane) with reactive groups at their ends and small trifunctional and tetrafunctional molecules. First we describe this polymerization system and our experimental methods. Then we use the branching theory to relate the viscosity rise data to the changing structure of the reacting system.

Table I
Reactants

c	formula	mol wt M_n	M_w/M_n (GPC)
B_2	$ViPhCH_3SiO(Si(CH_3)_2O)_n$-$SiCH_3PhVi$	11600[a]	2.21
B_2'	$ViPhCH_3SiO(Si(CH_3)_2O)_n$-$SiCH_3PhVi$	33400[b]	2.60
A_4	$(HSi(CH_3)_2O)_4Si$	329	
A_3	$(HSi(CH_3)_2O)_3SiPh$	330	
A_2	$H(CH_3)_2SiOSi(CH_3)_2H$	134	

[a] By vinyl titration (ref 14); average of six titrations ranging from 11 200 to 12 000. [b] Same as *a* with three titrations ranging from 31 500 to 34 800. [c] Reactant identification.

Experimental Section

The Chemical System. Polymerization between long molecules of end-vinyl-substituted poly(dimethylsiloxane) and silanes of three different functionalities were studied. A complete listing of the chemicals used, together with their average molecular weights and molecular weight distributions, is given in Table I. As an example, the reaction between the vinyl-terminated

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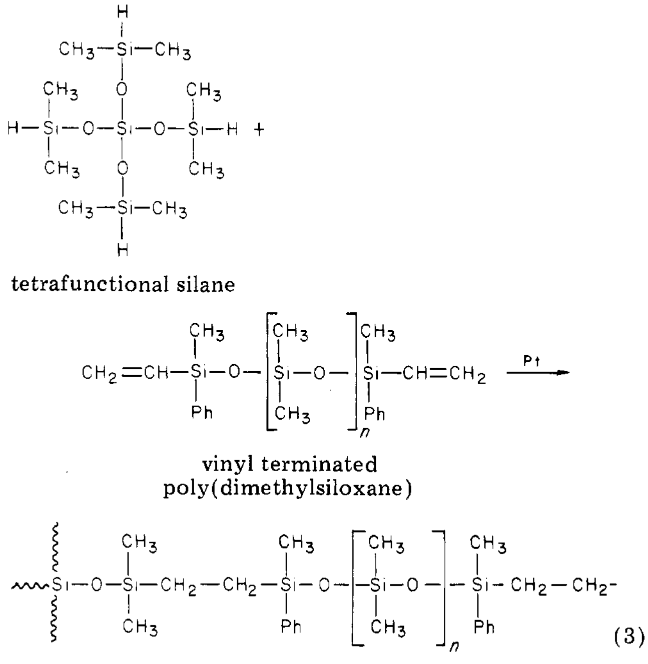
poly(dimethylsiloxane) and the tetrafunctional silane is shown below. For simplicity we will identify this reaction as $A_4 + B_2$.



(3)

The other two systems studied were the reaction between the trifunctional cross-linking agent and the vinylpoly(dimethylsiloxane) ($A_3 + B_2$) and the linear polymerization ($A_2 + B_2$), as indicated in Table I.

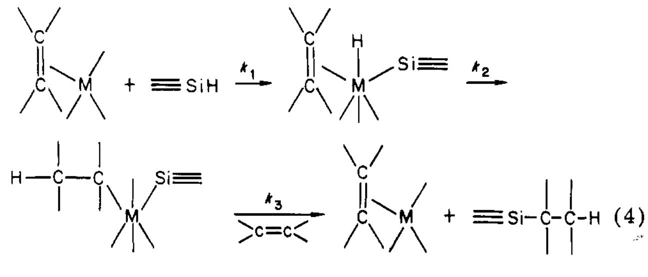
All the reactants in Table I were provided by the Dow Corning Corp. The vinylpoly(dimethylsiloxane) was prepared by equilibration of a mixture of cyclic siloxane tetramer (D_4) and bis(phenylmethylvinyl)siloxane [$(PhCH_3ViSi)_2O$].[12]

$$n((CH_3)_2SiO)_4 + (PhCH_3ViSi)_2O \rightarrow \text{polymer} + D_m$$

This method gives high molecular weight, end-blocked polymer together with some cyclics from D_4 to D_{20} and unreacted $(PhCH_3ViSi)_2O$. The lower boiling siloxanes together with the unreacted monomer were removed from the final mixture by vacuum stripping. This procedure yields more than 99% vinyl termination. Thus we believe that the content of monofunctional molecules in the poly(dimethylsiloxane) samples is less than 1%.[13] From size exclusion chromatography (GPC) the amount of nonfunctional cyclics remaining in the vinylpoly(dimethylsiloxane) was 5% by weight of the total. Since this study was completed we have found that nearly all of these cyclics can be removed by placing samples in a vacuum oven at ~100 °C for 1 week.

The molecular weight distribution of B_2 was also determined by GPC and the number average molecular weight was calculated by titration of the end vinyl groups with mercuric acetate.[14] GPC data was not corrected for spreading and thus the GPC M_n values are believed to be less accurate than those from titration. The cross-linkers were found better than 99% pure by gas–liquid chromatography using a silicon (SE-30-OV-101) column.

The hydrosilation reaction shown in eq 3 is catalyzed by platinum(II), rhodium(I), and iridium(I) complexes.[15] The mechanism for the reaction shown in eq 4 has been suggested by Chalk and Harrod.[16] It requires that the metal ion both coordinate the olefin and cleave the Si–H bond. They report 90% conversion.



The catalyst that we have used is *cis*-dichlorobis(diethyl sulfide)platinum(II) prepared following the procedure described in ref 17. The yellow crystals obtained were dissolved in equal amounts of toluene and low molecular weight poly(dimethylsiloxane). The concentration of the catalyst solution was 1–2% by weight in platinum. As the reaction does not proceed without catalyst it was initiated by bringing together, and carefully mixing and degasifying, equal volumes of two solutions. The first solution was made by dissolving the polyfunctional silane in the vinyl-terminated poly(dimethylsiloxane). The second solution was made of vinylpoly(dimethylsiloxane) plus catalyst. The overall platinum concentration was varied in the different experiments between 10 and 20 ppm. The total amount of solvent (from the catalyst solution) incorporated into the reactants with the catalyst was less than 2% by weight. The catalyst is poisoned instantaneously by traces of elemental sulfur. This effect was used to stop the reaction at desired points. It is important to note that the reaction is also inhibited by a variety of trace impurities, particularly sulfur-containing compounds. Occasionally a whole sample or a portion of a sample, for example, in contact with a rubber stopper, would not gel or form high polymer.

We believe that the chemical system we have used comes very close to fulfilling the ideal nonlinear polymerization conditions. The reactants have well-defined functionalities and the reaction should attain essentially complete conversion. No side reactions, byproducts, or isomerization has been detected using model compounds.[16] The silane groups on the cross-linker are sufficiently far apart to minimize substitution effects. The length of the vinyl-terminated poly(dimethylsiloxane) is high enough to greatly reduce the probability of loop formation.

Kinetic Measurements. The kinetics of the cross-linking reaction was followed by infrared spectroscopy. A single-beam instrument specifically designed for quantitative and kinetic studies was used (Wilks Model 80 spectrophotometer).[18] Two different absorbances were recorded: one at 2134 cm^{-1} corresponding to the strong band of the Si–H stretching vibration and the other one near 1970 cm^{-1}. The latter corresponds to a peak that remains unchanged during the reaction. It was employed as an internal standard to correct for the minor changes in the sample thickness on the different runs. The absorbance data were compared with digitally stored reference values, processed, and printed. Pure vinyl-terminated poly(dimethylsiloxane) was used to obtain reference values.

The reaction temperature was controlled at about 34 °C by a water-jacketed brass cell holder connected to a constant-temperature bath. The temperature in the cell was monitored by placing a thermocouple between the NaCl plates and was maintained within ±0.1 °C.

Linearity between absorbance and concentration, Beer's law, was verified for the Si–H peak using samples of known concentrations prepared by mixing both reactants without catalyst. The concentration of the mixtures used for the calibration ranged from 4 to 200 mol/m^3 of SiH.

Rheological Measurements. During the cross-linking reaction, the viscosity and first normal stress difference were followed continuously in the cone and plate geometry with a Rheometrics mechanical spectrometer.[19] Two different stress transducers were used, the standard one provided with the instrument and a new high-sensitivity transducer. With the former a cone of 0.06 radians, 72 mm, diameter was employed and the rotational speeds were varied between 1.0 and 0.001 rad/s. With the high-sensitivity transducer a cone of 0.04 radians, 50 mm, diameter was used with speeds from 0.1 to 0.004 rad/s.

The following procedure was used. After being mixed for 30 s with a motorized stirrer and degassed for 2 min with an aspirator, the reactants were placed simultaneously in the infrared spectrophotometer and in the mechanical spectrometer. The kinetics and the rheological properties were recorded. At the beginning of the reaction, when the viscosity was still low, high rotational speeds were used in order to obtain a torque signal high enough to be measured accurately. As shown in Figure 1, when the viscosity increased, the rotational speeds were reduced to keep them as low as possible. Normal forces were not detected until the reaction was very close to the gel point (p = 0.68 and 0.56 for the trifunctional and tetrafunctional systems, respectively). Then the increase in the normal force was almost explosive. If

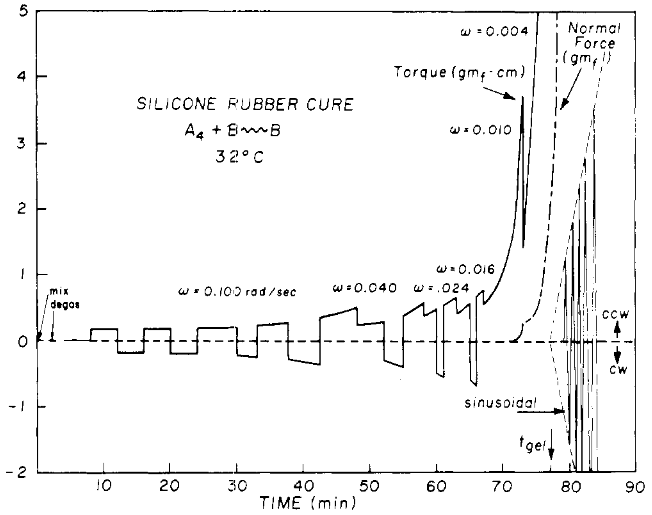


Figure 1. Typical output from the mechanical spectrometer showing the rise of the torque and normal force during the cross-linking reaction. Up to the gel point the data were obtained with steady rotation of the cone. Beyond the gel point small sinusoidal oscillations were applied to the fixture.

the rotation of the cone was maintained sample failure occurred. To avoid this the steady rotation of the fixture was changed to small strain sinusoidal oscillations when the normal force reached about 2.5 gm_f/cm^2. As shown in Figure 1, the oscillating torque was then recorded as a function of time. By extrapolation back to zero torque from these measurements, together with the point at which the normal force becomes greater than 1000 gm_f/cm^2, the experimental gel point was determined within ±30 s. This uncertainty in the gel time represents an inaccuracy of about ±0.003 in the determination of the extent of reaction at the gel point, p_{gel}.

Using two different transducers with the mechanical spectrometer permitted accurate measurement of the very large changes in viscosity (note Figure 2). The compliance of the sensitive transducer is large. Close to the gel point this may introduce errors. Thus the standard transducer was used in the gel region.

The shear rate dependence of the viscosities of several poisoned samples (see Table III) was also studied. The results (details are given in ref 20) show that, at the rotational speeds used in the experiments, the viscosities measured are the zero shear rate viscosities. We also verified that flow orientation did not effect the reaction kinetics. This was done by rotating the cone clockwise and counterclockwise and by letting the reaction proceed in the rheometer without rotation for periods of time of various length as indicated in Figure 1.

Theory

Several approaches have been developed to calculate relations between extent of reaction and molecular parameters in nonlinear stepwise polymerization. The basic theoretical concepts were established by Flory and Stockmayer.[21-24] Assuming equal reactivity of the functional groups and no intramolecular reaction between finite species, their derivations provide the basic expressions for the size and molecular weight distribution of the finite species as a function of the extent of reaction. In recent years two new approaches to the problem have been developed. The first by Gordon and co-workers[25-28] uses the theory of stochastic branching processes and requires deriving probability generating functions. The second by Macosko and Miller[29,30] uses the recursive nature of the branching process and elementary laws of probability.

Following the latter approach,[29] we have developed the following expression for the weight average molecular weight in a stepwise copolymerization between a reactant

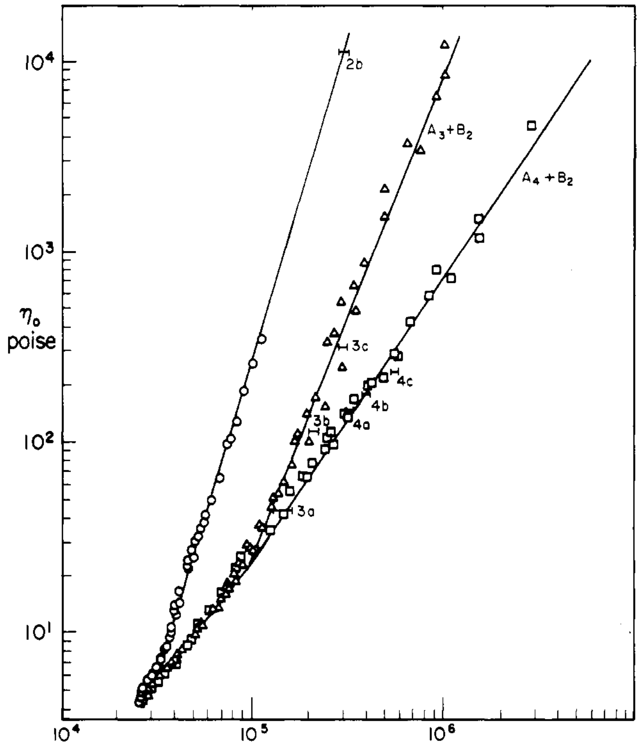


Figure 2. Log η_0 vs. log M_w plot for the three systems. The circles, triangles, and squares correspond to the results from the continuous runs. The bars correspond to the zero shear rate viscosities on the quenched samples. The width of the bars indicates the difference in the determination of the molecular weight from infrared (using eq 5) and light scattering (see Table III). For points 4a and 4c the bar indicates the light-scattering measurement uncertainty.

of functionality f, A_f, and a comonomer of functionality 2, B_2, where the B_2 is polydisperse.[31]

$$M_w = [(2r/f)(1 + rp^2){M_{A_f}}^2 + (1 - rp^2(f - 1)) \times M_{B_2,n}M_{B_2,w} + 4rpM_{A_f}M_{B_2,n} + 2rp^2(f - 1)M_{B_2,n},]^2/\{[(2r/f)M_{A_f} + M_{B_2,n}][1 - rp^2(f - 1)]\} \quad (5)$$

Here p is the extent of the reaction for the A groups, r is the stoichiometric imbalance of the reactants ($r = [A]_0/[B]_0$), M_{A_f} is the molecular weight of the A groups, and $M_{B_2,n}$ and $M_{B_2,w}$ are the number and weight average molecular weight of the B_2 groups.

In order to test our data against eq 2, we also need to calculate the radius of gyration ratio, g. Zimm and Stockmayer give g for random branching (ref 32, eq 42 and 43): for $f = 3$

$$g_3 = \frac{3(1 - 2\alpha)}{\alpha}\left[\frac{1}{2}\left(\frac{1 - \alpha}{\alpha}\right)\ln\left\{\frac{(1 - \alpha)^{1/2} + \alpha^{1/2}}{(1 - \alpha)^{1/2} - \alpha^{1/2}}\right\} - 1\right] \quad (6)$$

for $f = 4$

$$g_4 = \frac{1 - 3\alpha}{2\alpha}\ln\left(\frac{1 - \alpha}{1 - 3\alpha}\right) \quad (7)$$

where α is Flory's branching probability,[21,22] rp^2 for our case.

Physically the quantity gM_w is the weight average molecular weight of a linear chain with the same radius of gyration as the branched chain. This linear chain should be very close to the longest linear chain that we can pick out of the branched one. Recently we have derived an expression for the longest linear chain which passes through a B_2 group chosen at random on the branched

Table II
Gel Point

system	run no.	r	p_{gel} (exptl)[a]	p_{gel} (theor)
$A_4 + B_2$	1	0.999	0.581	0.578
	2	0.999	0.585	0.578
	3	1.003	0.588	0.577
	4	1.008	0.583	0.573
$A_3 + B_2$	1	0.999	0.703	0.708
	2	1.002	0.712	0.706
	3	1.008	0.710	0.701

[a] The inaccuracies in the experimental gel point are estimated to be ±0.010. This includes the measure of the gel time, the inaccuracy of the infrared, and the slight difference in the temperatures of the samples in the mechanical spectrometer and in the infrared spectrophotometer.

molecule.[31] The weight average molecular weight of this "longest chain" is

$$M_{\mathrm{L,w}} = M_{\mathrm{B_2,w}} + 2E(L_{\mathrm{B}}^{\mathrm{out}})M_{\mathrm{B_2,n}} \tag{8}$$

where the expected length of the chain looking out from one end of a B_2 chain is

$$E(L_{\mathrm{B}}^{\mathrm{out}}) = \sum_{l=0}^{\infty} P(L_{\mathrm{B}}^{\mathrm{out}} > l) \tag{9}$$

and the probability of a chain being longer than l is

$$P(L_{\mathrm{B}}^{\mathrm{out}} > l) = rp\{1 - [1 - pP(l_{\mathrm{B}}^{\mathrm{out}} > (l - 1))]^{f-1}\} \tag{10}$$

$$P(L_{\mathrm{b}}^{\mathrm{out}} > 0) = rp\{1 - (1 - p)^{f-1}\}$$

For our cross-linkers $f = 4$ or 3 and eq 8 can be readily solved. We expect that $gM_{\mathrm{w}} \simeq M_{\mathrm{L,w}}$ and compare both to our data below.

Results and Discussion

From the kinetics and rheological measurements, the extent of reaction and the viscosity rise vs. time were known for the different reacting systems. With eq 5 to 8 the evolution of the molecular parameters with time was calculated and related to the viscosity.

To verify that no intramolecular loops were formed and that all the chemical groups were equally reactive we measured accurately the extent of reaction at which gelation occurs. If either of these assumptions was violated or if the reactants were impure, a delay in the experimentally measured gel point should be found with respect to the theoretical one.[29]

$$p_{\mathrm{gel}}^2 = \frac{1}{r(f - 1)} \tag{11}$$

In Table II we report the results obtained for the experimental gel point of the two nonlinear reactions. The excellent agreement between theoretical and measured gel points confirms the ideality of the chemical system and shows the advantage of using long end-blocked reactive chains to minimize loop formation.

The validity of eq 5 for molecular weight from the extent of the reaction was also checked by reacting various mixtures up to near p_{gel} and then stopping the reaction by addition of elemental sulfur. After separation of the sulfur by centrifugation at 3500 rpm for 24 h, the extent of reaction of the samples was measured by infrared. The weight average molecular weight was determined with a KMX-6 Chromatix low-angle light-scattering photometer.[33] A series of four solutions of varying concentrations in toluene (1.0×10^{-5} to 5.0×10^{-5} gm/mL) was run for each polymer sample to extrapolate to infinite dilution. A 6.5° angle was used and linear plots were obtained. The results from these measurements in Table III show fairly good agreement between theory and experiment, although the light-scattering results were about 10% higher than the expected values. Light-scattering accuracy is estimated at ±5% due mainly to uncertainty in the change of index of refraction with concentration. It is possible that the sulfur stopped the reaction nonhomogeneously through the bulk sample.

Bulk viscosity data obtained from the study of the three reactions ($A_2 + B_2$, $A_3 + B_2$, $A_4 + B_2$) are given in tabular form by Valles.[20] A log η vs. log M_{w} plot from those data is shown in Figure 2. Viscosity and M_{w} (Table III) measured on the poisoned samples are also plotted on this figure showing good agreement with those values obtained from the continuous measurements.

Extrapolation of the straight line portions from the entangled and unentangled regions of the three systems yields M_{c}, the critical molecular weight for the onset of entanglement contribution, at $M_{\mathrm{c}} = 33\,000 \pm 7\,000$ for the linear system and $98\,000 \pm 10\,000$ and $110\,000 \pm 20\,000$ for the trifunctional and tetrafunctional systems, respectively. The corresponding viscosities at those points are 7.1, 23.5, and 26.0 P. The slopes at the different regions were calculated by least squares. In the calculations only the data points near M_{c} were used: $1.2M_{\mathrm{c}} \leq M_{\mathrm{w}} \leq 0.8M_{\mathrm{c}}$. The values for the slopes in the lower region, with a confidence interval of 95%, are 1.99 ± 1.4 for the linear system and 1.27 ± 0.04 and 1.30 ± 0.10 for the A_3 and A_4 branched systems, respectively. In the entangled portions of the plot the slopes are 3.39 ± 0.08, 2.59 ± 0.14, and 1.47 ± 0.17. The inaccuracy in the slope of the linear system in the nonentangled region is due to the fact that, at the beginning of the reaction, the molecular weight of that system is very close to M_{c}. Only a few data can be obtained before the critical molecular weight is reached.

Calculations of the weight average number of branching

Table III
Properties of "Quenched" Samples

system	sample	p (infrared)	η_0, P	$\overline{M}_{\mathrm{w}}$ (light scattering) $\times 10^{-3}$	M_{w} (from p and eq 5) $\times 10^{-3}$	g (from p and eq 6 or 7)
$A_2 + B_2$	2a			99		1.0
	2b		12000	303	285[a]	1.0
	2c			1000		1.0
$A_3 + B_2$	3a	0.641	50	179	134	0.576
	3b	0.665	120	232	207	0.470
	3c	0.679	300	321	305	0.382
$A_4 + B_2$	4a		145	328		
	4b	0.559	180	410	380	0.240
	4c		230	575		

[a] Estimated from viscosity.

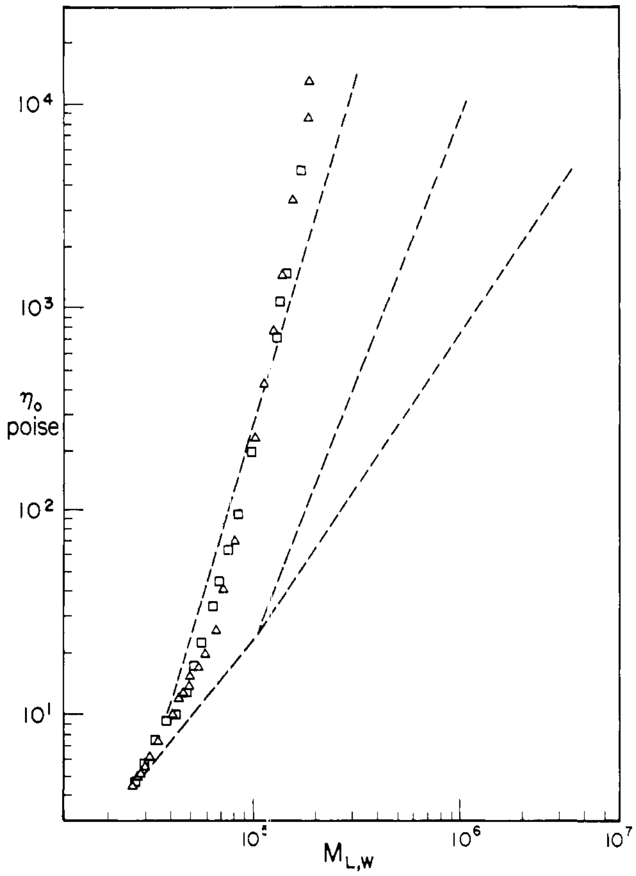


Figure 3. Log η_0 vs. log $M_{\mathrm{L,w}}$, the weight average molecular weight of the longest chain. Symbols are the same as in Figure 2. Dotted lines are the results from Figure 2, log η_0 vs. log M_{w}.

points and chains per molecule for branched systems as a function of the extent of the cross-linking reaction show that both are similar in the unentangled region.[20] At M_{c} for the $A_4 + B_2$ system, where the extent of reaction is $p = 0.51$, there are about four trifunctional branches for each tetrafunctional one. Thus the structure of this system does not differ at that point substantially from the trifunctional system. This is due to the fact that the fraction of tetrafunctional branches in the $A_4 + B_2$ system is given by p^4 while the fraction of trifunctional branches grows as $4(1 - p)p^3$ (ref 31).

It is interesting to note from Figure 2 the average molecular weight of the longest chain for the branched system is significantly higher at the break point than the average molecular weight of the linear system at the critical point (62000 vs. 33000). This seems to indicate that the presence of a small amount of branching (there is an average of two branches per molecule in both branched systems at the break point) affects significantly the ability of the polymer to become entangled.

Figures 3 and 4 compare the zero shear viscosity of the three systems with $M_{\mathrm{L,w}}$, the weight average molecular weight of the longest chain, and with gM_{w}. For both measures up to $M_{\mathrm{L,w}} \simeq gM_{\mathrm{w}} \simeq 10^5$, the viscosity data for the tetrafunctionally branched samples is brought into fairly good agreement with the data for the linear ones in accordance with eq 2. The trifunctionally branched samples still show somewhat lower viscosities in this region. Above 10^5 the branched samples show viscosity enhancement in both Figures 3 and 4 similar to that reported by Graessley for star-branched polyisoprenes.[11]

Conclusions

The reaction of vinyl-terminated poly(dimethylsiloxane) chains with multifunctional silanes appears to satisfy the condition for ideal nonlinear step polymerization. With three- and four-functional silanes we have determined accurately the onset of gelation and found remarkable agreement with the values calculated from the branching theory. M_{w} calculations from the branching theory using infrared to measure the extent of reaction also give reasonable agreement with our experimental M_{w} values. These results are important confirmations of the branching theory for nonlinear polymerization.

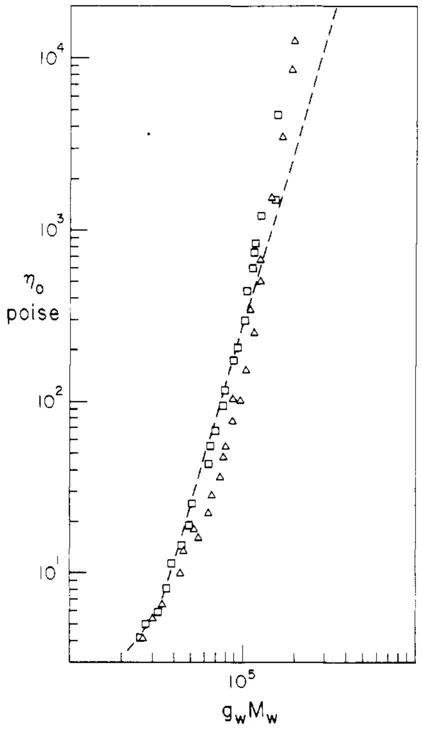


Figure 4. Log η_0 vs. log gM_{w}; symbols are the same as Figure 2.

Zero shear viscosity for the linear polymerization was found to follow $M_{\mathrm{w}}^{3.4}$. The branched polymers had lower but also constant exponential dependence upon M_{w}. Viscosity data on both linear and branched molecules are brought together when plotted vs. gM_{w}. Beyond $gM_{\mathrm{w}} \simeq 10^5$ the branched samples show an enhanced viscosity. These results are in agreement with the literature on star-branched and fractions of randomly branched polymers. The weight of the longest linear chain, $M_{\mathrm{L,w}}$, also reduces the viscosity data as well as gM_{w}. We are presently investigating theoretically these two measures of branched molecules.

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Theoretical Study of Living Polymerization Reactions Involving a Transfer Agent

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ABSTRACT: In the present paper, a theoretical study is made of the effect of a transfer agent on the molecular size distribution in living polymers, assuming an infinitely fast initiation and instantaneous reinitiation after the transfer reaction. Expressions for the number-average and weight-average chain lengths are obtained for three cases: (a) both the monomer and the transfer agent remain at constant concentration, (b) only the concentration of the transfer agent is kept constant, and (c) both concentrations vary with time. The last one is the usual situation, but the circumstances under which approximate solutions corresponding to constant concentration of transfer agent could be safely used are discussed in detail.

In living polymerization, when initiation is instantaneous and transfer is absent, the resulting material has a narrow Poisson distribution[1] of chain lengths. Broadening of the distribution can be due to different factors such as impurities, transfer to monomer, slow initiation, depropagation, etc. Szwarc and Litt[2] and also Coleman et al.[3] have studied the molecular weight distribution for ionic polymerizations in which there exist termination reactions, either spontaneous or due to impurities. Similarly, Orofino and Wenger[4] and Figini[5] studied such systems with bifunctional initiators. Many workers[6-8] have considered mathematically the effect on the molecular weight distribution of a slow initiation. In those ionic polymerizations in which two species contributing to the chain growth can coexist, the polydispersity ratio increases, as shown by Szwarc and Hermans,[9] Coleman and Fox,[10] and Figini.[11] Still another factor which can affect the distribution is reversibility of the propagation step, mathematical study of which was carried out by Brown and Szwarc[12] and by Miyake and Stockmayer.[13] More recently, Nanda and Jain[14,15] have studied the distribution of molecular weights in ionic polymerizations with spontaneous transfer and transfer to monomer.

So far, however, no study is known, at least to these authors, of the distribution in ionic polymerizations in which there exists a transfer reaction involving a species present in the mixture or formed in the initiation step and in which, at the same time, an instantaneous reinitiation takes place. Rozenberg and co-workers[16] have experimentally studied the polymerization of tetrahydrofurane with trialkyloxonium salts, including water as transfer agent, and observed that the polymerization rate remains constant while the polydispersity index increases with the transfer agent concentration. It therefore seemed worthwhile to discuss this problem, and we report here the averages obtained for different cases from an appropriate kinetic scheme. We hope the results will be useful for checking against experimental findings and for providing increased understanding of the factors governing a living polymerization.

Kinetic Scheme and the Averages

The kinetic scheme we considered is analogous to those in ref 4 and 5, the only difference being the inclusion of a transfer agent in the corresponding step. It involves three stages: initiation:

$$\mathrm{I} + \mathrm{M} \xrightarrow{k_i} \mathrm{N}_1{}^*$$

propagation:

$$\mathrm{N}_i{}^* + \mathrm{M} \xrightarrow{k_p} \mathrm{N}_{i+1}{}^*$$