

Ultrasonic Degradation of Polysiloxane Solutions

M. T. SHAW* and F. RODRIGUEZ,

School of Chemical Engineering, Cornell University, Ithaca, New York 14850

Synopsis

Fractions of dimethylsiloxane polymer with viscosity-average molecular weights from 2.4×10^5 to 1.3×10^6 were dissolved in toluene in concentrations from 0.01 to 1.0 g./dl. These solutions were subjected to ultrasonic degradation at 20,000 cps for periods extending to as much as 960 min. in a water-cooled reaction vessel. Gel permeation chromatography shows that samples with different initial distributions approach the same distribution after 120 min. of degradation. Dilution of the polymer from 1.0 to 0.01 g./dl. more than triples the degradation per gram of polymer but requires 10 times as much energy per gram of polymer to degrade from a number-average molecular weight of 10^6 to 10^5 . Increasing the power input from 36 to 72 w. almost doubles the degradation rate per gram of polymer.

Introduction

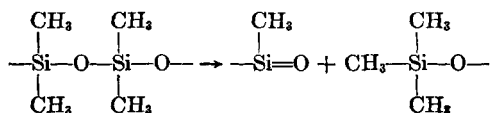
Ultrasonic degradation of a polymer refers to a lowering of molecular weight when a solution of a polymer is subjected to irradiation with ultrasonic energy. This molecular weight lowering is permanent, resulting from scissions in the polymer chain.

Although a great deal of effort has been expended in studying the kinetics of ultrasonic degradation of polymer systems, only a few workers have attempted to follow the distribution of molecular weights during the course of degradation. The reason for this is that the common method of making an analysis of a distribution involves fractional precipitation of the polymer with a nonsolvent, followed by characterization of the fractions, a tedious and uncertain procedure.

The advent of gel permeation chromatography (GPC) has changed the picture somewhat. With GPC it is possible to obtain quickly a distribution with good relative accuracy. That is to say that, although the distribution given by GPC is not absolute, a comparison of any two distributions should show accurately any differences between the two. It was with this spirit that work was begun in an attempt to characterize changes in the distribution of silicone polymer when solutions of the polymer were subjected to ultrasonic irradiation. Also the effect of important variables, such as concentration, initial distribution and power input on such changes were studied.

* Present address: Department of Chemistry, Princeton University, Princeton, New Jersey.

The literature concerning ultrasonic degradation has been reviewed and criticized in several places.¹⁻⁴ Several studies have dealt specifically with degradation of polysiloxanes. Berlin and Dubinskaya,⁵ working with molecular weights of around 500,000, obtained relatively slow degradation of poly(dimethyl siloxane) in toluene solution with concentrations ranging from 0.1 to 5 g./dl. They found that degradation did not proceed by a radical mechanism as is the case for a majority of other systems studied (e.g., polystyrene,⁴ cellulose nitrate⁶) where the presence of radicals was confirmed by the consumption of the free-radical scavenger, diphenyl picryl hydrazyl (DPPH). Berlin and Dubinskaya proposed a nonintermediate type disproportionation:



Thomas and DeVries,⁷ also working with poly(dimethyl siloxane), confirmed the absence of radicals with DPPH. They found also that methanol, a good nucleophile, was consumed and thus proposed a heterolytic cleavage of the Si—O bond. In the absence of methanol, degradation was only slightly slower, and they suggested that impurities in the solvent, such as air, would act as nucleophilic species. In the complete absence of such species, they suggested disproportionation (in agreement with the scheme of Berlin and Dubinskaya) to account for the degradation observed.

In the present work methanol was not added, but the toluene solutions were saturated with air at room temperature. The disadvantage of adding methanol as a scavenger for radicals is that it also makes the solvent poorer for silicones in the sense that polymers coil more tightly. In fact, addition of one volume of methanol to three of a toluene solution of poly(dimethyl siloxane) is sufficient to precipitate high molecular weight species. It has been observed in the mechanical degradation of polyisobutylene by high-speed stirring that the polymer degrades more rapidly in a poor solvent than in a good one.⁸ Thus, addition of methanol might accelerate degradation for several reasons. Moreover, since Thomas and DeVries found only a slight increase in rate of degradation with methanol addition, it is believed that in the present work, radical recombination is a minor factor.

Gel permeation chromatography work with silicones has been reported recently.⁹ Early work on the GPC has been summarized by Porath and Flodin,¹⁰ Moore,¹¹ and Determann.¹² Technical articles by Waters Associates, Inc., Framington, Mass. also contain much basic information. Mathematical models for GPC distributions have been developed by Hess and Kratz,¹³ Tung,¹⁴⁻¹⁶ and Rodriguez and Clark.¹⁷

Experimental

A Biosonik sonic generator (Model GW-2), manufactured by Blackstone Ultrasonics, Sheffield, Penn., was used as the source of energy for degradation of the polymer solutions. This is a magnetostrictive device capable of

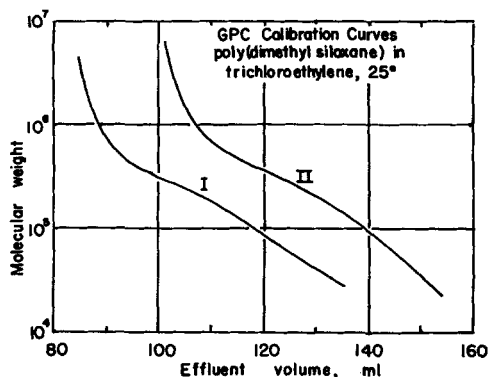


Fig. 1. Calibration curves for two GPC arrangements: (I) four columns rated at 3×10^3 , 3×10^4 , 10^6 , and 10^8 A.; (II) four columns rated at 10^6 , 3×10^4 , 10^8 , and 10^8 A.

an average output of 120 w. at a constant frequency of 20,000 cps. The magnetic core of the machine is equipped with a $\frac{3}{8}$ -in. diameter probe which can be dipped into the polymer solutions from above. Two concentric cylinders were soldered together to form a reaction vessel with a jacket for cooling water. The inner vessel had a total capacity of about 250 ml. Solution temperature could be maintained at 23–25°C. In some prolonged runs temperatures reached 30°C. and there was measurable evaporation.

The gel permeation chromatograph used for distribution analysis is described in detail elsewhere.⁹ Typical calibration curves based on poly-(dimethyl siloxane) fractions (Fig. 1) resemble those reported earlier.⁹ Trichloroethylene at a flow rate of 1.1 ml./min. and 25°C. was used as the eluent through the four-column arrangements and then through a sodium chloride flow cell in a Beckman IR-10 infrared spectrophotometer. The infrared absorbance at 9.3 μ was used as a measure of concentration of siloxane in the effluent.

Viscosities were determined in a Ubbelohde capillary viscometer at 25°C.

A poly(dimethyl siloxane) gum stock (furnished by Union Carbide Corporation Silicones Division) was fractionated into six parts by precipitation from toluene with methanol. The resulting distributions for the four fractions used in this study are summarized in Figure 2. Degradation was carried out at concentrations of 0.01–1.0 g./dl. in toluene. Each determination of molecular weight or distribution represents a separately irradiated 50-ml. sample rather than successive withdrawals from a single run which would have changed the volume being irradiated. Since only 1 mg. of siloxane is needed for a GPC run, more concentrated samples were injected directly. Toluene elutes after the siloxane in the GPC and gives a distinct and well-separated peak. Samples with siloxane concentrations of 0.01 and 0.05 g./dl. had to be concentrated by evaporation of solvent or by precipitation from toluene with methanol.

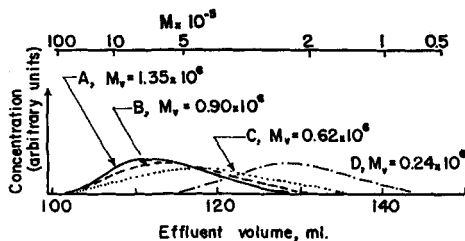


Fig. 2. Distributions for the fractions of poly(dimethyl siloxane) as determined in the GPC with column system II.

Results and Discussion

In preliminary work, the viscosity-average molecular weight \bar{M}_v was followed as a function of degradation time, power input, and initial molecular weight. It became apparent that plots of \bar{M}_v superpose if the product of power and time (energy input) is used as the correlating variable rather than time alone. When polymers of widely different initial molecular weight are degraded for long times, the \bar{M}_v -time (energy) plots converge (Fig. 3). The general picture is in qualitative agreement with previous studies. However, Figure 3 does not support the concept of a limiting molecular weight. If an arithmetic scale is used for energy rather than the logarithmic scale, a reversed S-shaped curve with an apparent limiting \bar{M}_v can be constructed. The value of the limiting \bar{M}_v thus obtained is a function of the size of arithmetic scale employed.

The converging of results for various initial molecular weights raises questions as to the distributions of the fractions at this point in the degradation process. Unfortunately, viscosity-average molecular weight has its limitations. For instance, it cannot be used meaningfully for kinetic analysis because it has no regular relationship to the number of breaks or chain scissions experienced by the polymer mass. Also it tells nothing about the distribution of molecular weights. The viscosity work does

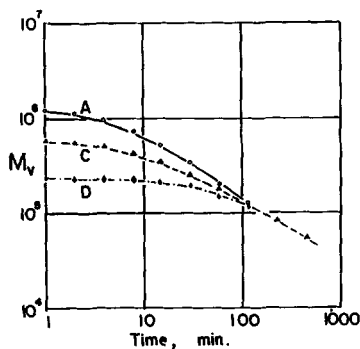


Fig. 3. Course of degradation followed by viscosity-average molecular weight \bar{M}_v for samples A, C, and D. Concentration, 1.0 g./dl.; power level, 36 w.

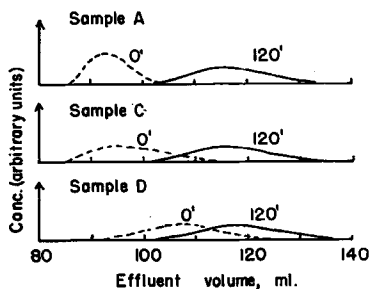


Fig. 4. GPC analysis of undegraded fractions and the same after 120 min. under the conditions of Fig. 3 (column system I).

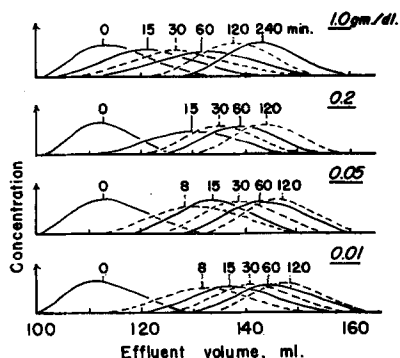


Fig. 5. Course of degradation followed by GPC analysis for four concentrations of fraction B (column system II).

show, on the other hand, that smooth degradation can be expected and that the degradation conditions are fairly constant.

An analysis by GPC of the degraded fractions of Figure 3 confirms that not only is \bar{M}_v the same for all three, but that the distributions are indistinguishable (Fig. 4). *A priori* reasoning might have postulated a broader distribution for the degraded sample of high initial \bar{M}_v . It is apparent that the long-term degraded samples are not particularly broad in distribution in any case; particularly, there is no low molecular weight tail as might be expected from a completely random process.

The GPC is useful in following the course of degradation (Fig. 5). Since the irradiation is not homogeneously distributed throughout the reaction vessel, the broad distributions at short degradation times are reasonable. On the other hand, there is no evidence of bimodal distributions, even at very short times. There is a possibility that the GPC analysis model proposed by Tung¹⁴⁻¹⁶ would resolve such features, but it was not applied here. In all these generalizations one must bear in mind the limits of resolution of the GPC. Fortunately, the distributions of greatest interest coincided with the region of maximum sensitivity for the apparatus.

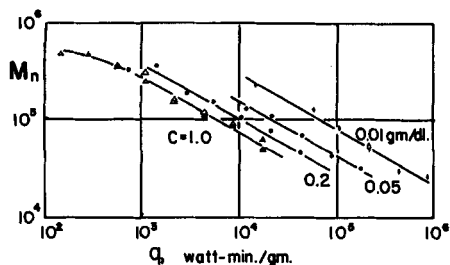


Fig. 6. Number-average molecular weights derived from GPC curves correlated with q , the product of time and power per gram of polymer.

Dilute solutions degrade more rapidly than do more concentrated ones. El'tsefon¹⁸ suggested that degradation could be correlated on the basis of a q -factor where

$$q = \frac{(\text{intensity of radiation}) (\text{degradation time})}{(\text{volume of sample}) (\text{concentration of polymer})}$$

The units of q are watt-minutes/gram or total energy input per gram of polymer. When \bar{M}_n calculated from the GPC data is plotted on this basis (Fig. 6), the effect of concentration is overcorrected. Superposition would be best if the product of q and $(\text{concentration})^{1/2}$ were used. The use of q is hard to defend because the total input of energy in the system far exceeds that necessary to break bonds. Figure 6 does show that more energy will be required, with the apparatus at hand, to bring the molecular weight of 1 g. of polymer down to a certain level if the concentration is decreased from 1.0 to 0.01 g./dl. This is logical because at low concentrations more energy is apt to be dissipated in directions other than bond breaking.

It is of interest to try to extract from the data some rate constants based on admittedly oversimplified kinetic schemes. One such scheme assumes the rate of bond breakage to be a first-order reaction. Let B equal the total number of breakable bonds in a system. This is a large number which is proportional to total polymer concentration and which does not change appreciably with degradation. If we degrade from a degree of polymerization of 10^5 down to 10^4 , we need break only 1 bond out of 10^4 , changing the total number of intact bonds insignificantly. But dB/dt , the rate of change of B with time t is proportional to $d(1/\bar{M}_n)/dt$, where \bar{M}_n is the number-average molecular weight; that is, each bond breaking raises the number of molecules present and lowers the \bar{M}_n . We now assume that the bond-breaking rate is first-order in bond concentration B and that the rate constant is proportional to the average weight raised to a power a .

$$dB/dt = -(kM^a)B \quad (1)$$

B is relatively constant, though proportional to concentration, making this a pseudo zero-order reaction. We can identify M of eq. (1) with \bar{M}_n . Combining equations gives

$$d(1/\bar{M}_n)/dt = -KM_n^a \quad (2)$$

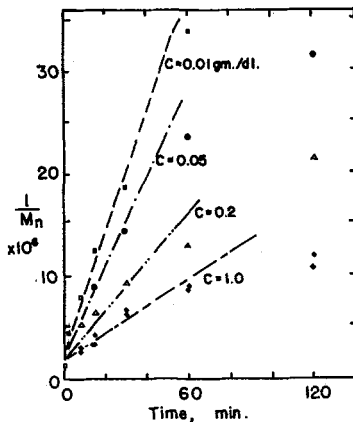


Fig. 7. Attempted correlation of degradation for kinetic scheme based on random scission [eq. (4) with $a = 0$].

This can be integrated between the limits $t = 0$ and $t = \theta$:

$$\int_{\bar{M}_n(0)}^{\bar{M}_n(\theta)} (1/\bar{M}_n)^{1+a} d(1/\bar{M}_n) = -K \int_0^\theta dt \quad (3)$$

$$[1/\bar{M}_n(\theta)]^{1+a} - [1/\bar{M}_n(0)]^{1+a} = K\theta \quad (4)$$

If scission is random ($a = 0$), this reduces to the case reported by Mark and Tobolsky¹⁹ which is applicable to a degradative process such as hydrolysis. A plot of $1/\bar{M}_n$ versus time (θ) is not linear for ultrasonic degradation (Fig. 7). An idea of the correct value for the parameter a can be obtained under conditions where $\bar{M}_n(\theta) \ll \bar{M}_n(0)$. When the second term in eq. (4) can be neglected, we have

$$[1/\bar{M}_n(\theta)]^{1+a} = K\theta$$

or

$$(1 + a) \log \bar{M}_n = -\log K - \log \theta \quad (5)$$

A plot of $\log \bar{M}_n$ versus $\log \theta$ (or $\log q$) such as Figure 6 does appear to reach a slope of $-1/2$ to $-2/3$. This corresponds to values of $a = 1$ and $1/2$, respectively. A dependence of the rate of bond breaking on molecular weight to such a low power is not unreasonable and is of the same order of magnitude as the dependence of dilute solution viscosity on molecular weight. This, in turn, suggests a hydrodynamic mechanism. Unfortunately, hydrodynamic reasoning predicts a much higher dependence on concentration than is observed.

As another approach, the experimental data can be fitted by first-order kinetics if one assumes a "limiting" molecular weight below which degradation does not occur. The disadvantage of such a method is that there is for each concentration a different limiting molecular weight. The

method chosen here expresses the order by the parameter a in eq. (1). As shown before, this parameter does not vary with concentration.

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Résumé

Des fractions d'un polymère diméthylsiloxanique de poids moléculaire moyen viscosimétrique de 2.4×10^6 à 1.3×10^6 ont été dissoutes dans le toluène à des concentrations variant de 0.01 à 1.0 gr./dl. Ces solutions ont été soumises à dégradation ultrasonique sous 20.000 cycles/sec. pour des périodes allant jusque 960 min. dans un récipient refroidi par l'eau. La chromatographie par perméation sur gel montre que les échantillons de différentes distributions initiales se rapprochent de la même distribution après 120 min. de dégradation. La dilution du polymère de 1.0 à 0.01 gr./dl. triple au moins la dégradation par gramme de polymère et requiert au moins dix fois plus d'énergie par gramme de polymère dégradé d'un poids moléculaire moyen en nombre de 10^6 à 10^8 . En accroissant l'énergie de 36 à 72 watts, la vitesse de dégradation double environ par gramme de polymère.

Zusammenfassung

Fraktionen eines Dimethylsiloxanpolymeren mit Viskositätsmittelwerten des Molekulargewichtes von $2,4 \times 10^6$ bis $1,3 \times 10^6$ wurden in Toluol zu Konzentrationen von 0,01 bis 1,0 g/dl gelöst. Diese Lösungen wurden in einem wassergekühlten Reaktionsgefäß für Zeiträume bis zu 960 min einem Ultraschallabbau bei 20000 Hz unterworfen. Der Gelpermeationschromatograph zeigt, dass sich Proben mit verschiedener Anfangsverteilung nach einem Abbau während 120 min der gleichen Verteilung nähern. Ver-

dünnung des Polymeren von 1,0 auf 0,01 g/dl liefert einen mehr als dreifachen Abbau pro Gramm Polymeres, erfordert aber eine zehnmal so grosse Energie pro Gramm Polymeres, um einen Abbau von einem Zahlenmittel-Molekulargewicht 10^6 auf 10^5 zu bewirken. Eine Erhöhung der Leistungsaufnahme von 36 auf 72 W gibt fast eine Verdopplung der Abbaugeschwindigkeit pro Gramm Polymeres.

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